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ASSESSING THE IMPACT OF
HAZARDOUS IMMISCIBLE
LIQUIDS IN SOIL

R. A. C. PROJECT NO. 104 PL

Report prepared for Environment Ontario by:

G.J. Farquhar, E.A. McBean
Civil Engineering
University of Waterloo
and
R.G. Pearson
Air Resources Branch

APRIL 1990



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ASSESSING THE IMPACT OF HAZARDOUS IMMISCIBLE LIQUIDS IN SOIL

G.J. Farquhar, E.A. McBean and R.G. Pearson

EXECUTIVE SUMMARY

The presence of hazardous immiscible liquids in soil is one of today's most troublesome environmental problems. Such liquids include chlorinated solvents and petroleum products which enter the soil from spills, improper disposal sites, and leaks from tanks and pipelines. Unfortunately, society's ability to respond to such problems is impeded by its limited understanding of the behavior of immiscible liquids in soil. As a result of this situation, a research programme to study the fundamentals of immiscible liquid movement in soil was undertaken in Civil Engineering at the University of Waterloo. Funding for this project was provided in large part by the Ontario Ministry of the Environment.

The research programme focussed on three major subjects; the formation of spills including penetration into the soil, the movement of liquids through soil, and the behavior in soil of vapours released from the liquids. It approached the work from two points of view; the development of mathematical models based on theory to simulate liquid and vapour movement and the performance of laboratory scale experiments to collect data for verifying theory and testing models. The programme spanned three years, produced a series of technical papers, and provided financial support for six post graduate students.

Three computerized mathematical models were produced and tested on a limited scale against laboratory data. The models included two spill simulation models, a model for liquid movement in soil, and one for

vapour transport in soil. Tests showed that each was capable of providing reasonable simulations of the laboratory data. Detailed evaluation of the models with respect to field conditions is being done in subsequent work.

Experimentation was carried out by spilling immiscible liquids onto soil and other surfaces, by allowing liquids to penetrate through soil, and by releasing vapours in soil and tracking their movement. Other supporting experiments were also done. Examples of these included relative permeability and capillary pressure measurements for multiphase soil/water/immiscible liquid systems. Liquids used included hexane, kerosene, pentane, mineral oil and others to a lesser degree. In many cases, the experiments performed were among the first of their kind. For most experiments, equipment and techniques had to be developed specifically for this work. The "thermoprobe" used to measure the relative concentration of water and immiscible liquid in soil is an example of the equipment produced during the study.

The research done in this project is important for several reasons:

1. The results have contributed significantly to understanding the fundamentals of immiscible liquid flow over and within soil.
2. Experimental equipment and methods have been produced and are available for subsequent research projects.
3. A data base involving two soils and several liquids is now accessible to scientists and practitioners to assist them in other aspects of the problem. The data base also provides a means, previously severely limited, with which to validate mathematical simulation models.

4. Four simulation models have been developed and can be used in many ways, for example to assess contaminant movement problems in the field and to evaluate remedial measures. Some models require additional refinement but others such as the Vapour Transport Model have already been successfully applied to field situations.
5. Several students, both postgraduate and undergraduate engineers, have worked on this project and are now a part of the professional force working on problems with immiscible liquids in the environment.

The research begun in this project is now continuing at the University of Waterloo under a new Funding Grant provided by the Ontario Ministry of the Environment. The work is being done by the Department of Civil Engineering in co-operation with the Department of Earth Sciences. It involves replicating and extending existing experimentation, validating models and applying them to field situations, assessing remedial technologies, and examining phase transfers of contaminants between the liquid, soil water, and the gaseous environment. The results of this new research will be made available through publication and presentation at technical conferences.

ACKNOWLEDGEMENT

The research described herein was funded by the Ontario Ministry of the Environment during the period from April, 1984 to March, 1987. The principal investigators, Professors G. Farquhar and E. McBean, gratefully acknowledge this support. They are also indebted to the Technical Liaison Committee, especially its Chairman, Mr. R. Pearson, for his interest in the work, his thoughtful guidance, and his patience in seeing the work to completion.

Technical Liaison Committee Members:

P. Belling
G. Hughes
J. Lye
A. Scott
R. Pearson, Chairman

1. INTRODUCTION

The presence of hazardous chemicals in soil and groundwater has been of great concern to our society over the past two decades. The threat to water supply systems, the incidence of soil contamination and plant uptake and the growing anxiety over harmful vapours migrating into inhabited regions have given rise to these concerns. Hazardous chemicals appear in soil and groundwater as a result of accidental spills, deliberate discharges and leakage from disposal sites. While tighter control is being imposed on these sources, complete control does not presently exist nor is it likely to in the near future. Consequently, understanding the behavior of hazardous chemicals in soil and groundwater and their response to remedial measures is essential for the protection of hydrogeologic environments.

Hazardous immiscible liquids (HIL) make up a group of contaminants frequently associated with spills and inadequate disposal sites. Chlorinated hydrocarbons such as polychlorinated biphenyls (PCB's) and trichloroethane (TCE), petroleum products, for example gasoline, and solvents including benzene and methylene chloride are common examples of spilled or improperly disposed of HIL.

The fact that these liquids are immiscible presents a special set of problems. Miscible and soluble contaminants become a part of the aqueous phase and thus move as the groundwater moves although retardation may occur. Immiscible liquids remain separate from the groundwater and thus may move and behave differently. Predicting their rates of migration, their responses to remedial measures such as pumping and even detecting their presence is much more difficult than for aqueous phase contaminants. Volatile HIL create an additional problem

through the evolution of hazardous vapours to the unsaturated soil gas space and eventually to the atmosphere.

The large majority of research conducted on the contamination of soil and groundwater has dealt with aqueous phase contaminants. Very little has been done with immiscible contaminants or the vapours which they produce either in terms of their movement and retention in soil or their response to remedial measures. Virtually no quantitative data are available. Considering the frequency with which HIL are spilled or leaked to hydrogeologic environments, this represents an important area of research need.

As a consequence of this need, the research described herein was undertaken to study the behavior of HIL in soil. It was designed to provide a clearer understanding of HIL movement and retention, vapour evolution and migration, detection, and response to control measures. The research programme extended over a three year period ending in March, 1987 under sponsorship from the Ontario Ministry of the Environment.

The Proposal which provided the basis for funding the project identified four major topics for the study of HIL:

- A. The spilling of HIL onto soil and other surfaces with accompanying penetration and vaporization.
- B. The movement of HIL in soil with varying degrees of water saturation.
- C. The release of vapours from HIL in soil and the subsequent movement of vapours in soil and release to the environment.
- D. The development of a computer-based, spill management model to provide rapid information feedback to assist remediation work.

The initial three topics became the focus of the project. The fourth was abandoned because of time and financial constraints, delay due to the requirement for results from the prior topics as input, and similar work being done elsewhere.

It was proposed that the research be conducted with four major activities:

- A. Reviews of relevant literature.
- B. Development of mathematical models to simulate spills with vaporization and infiltration, HIL movement through variably saturated soil and vapour transport through soil with discharge to the atmosphere.
- C. Establishment of experimental equipment and methods and subsequent experimentation with spills, HIL movement through soil and vapour behavior in soil.
- D. Corroboration by simulating experimental results through the use of the mathematical models produced.

This Technical Summary provides a synopsis of all research activities undertaken in the project. It also serves as a guide to the detailed information presented in seven Technical Reports prepared to describe the various components of the research. Descriptions of these seven Reports are presented subsequently in Section 7 of this document.

2. SIMULATION MODEL DEVELOPMENT: A RATIONALE

At the outset of this research very little quantitative information was available on the behavior of HIL in soil. This applied to both field and laboratory investigations. It was especially the case for soil/contaminant interactions, relationships for permeabilities and capillary pressures for variably saturated, multifluid systems and the spreading and infiltration of spilled liquids onto soil. It also did not appear that this kind of quantitative data would be available in the near future. Consequently, it was decided that the development of mathematical simulation models should be a part of this research in order to study immiscible fluid behavior more extensively.

Mathematical models are simplified representations of physical phenomena. However, within the constraints of the underlying assumptions, these models can be used to examine a range of conditions which would not be feasible to investigate on an experimental basis.

Simulation models were an essential part of this project because, once properly tested and calibrated, they can be used:

- A. to examine immiscible liquid behavior over a wide range of soil and liquid properties, field and environmental conditions, spill configurations, etc. for which individual equivalent experimentation would be extremely expensive,
- B. to test the sensitivity of liquid behavior to ranges of specific input parameter values,
- C. to extend documented trends at existing spill sites, and
- D. to assist in the management of spills by evaluating responses to various proposed remedial measures.

Three sets of simulation models were produced either in whole or in part in the context of this project:

- A. Spill Simulation Model (Wall, 1984, TR2)
- B. Two Phase Porous Media Flow Model (Osborne 1984, TR4)
- C. Vapour Transport in Soil Model (Allan, 1985, TR6).

All models have as their core, computerized numerical solutions to the partial differential equations which describe the various fluid transport systems. All models have been completed to the point where computer codes have been prepared and verified with analytical solutions. All models have experienced limited testing using laboratory or field data against which to make comparisons. As a part of this project, experimentation was carried out to provide data for comparison with simulation model results.

3. SPILLS OF IMMISCIBLE LIQUIDS ONTO SOIL

One phase of the project was committed to the study of HIL behavior when spilled onto soil and other surfaces. It was designed to study and to quantify the spreading, penetration and evaporation of HIL on various surface configurations. Little prior data were available and yet were considered necessary for understanding and responding to spill situations. Thus, a research programme involving spill simulation model development and experimentation was undertaken.

Approximately 45 experiments were conducted (some in conjunction with the firm of S.L. Ross, Ottawa, Ontario) in which various liquids were spilled onto surfaces both flat and inclined and either impervious or sodded. Liquids were selected to exhibit a range of viscosities and mass densities. Measurements were made to determine spill size, shape and rate of expansion as well as infiltration. Two computer-based mathematical models (Wall Model and MBPF Model) to simulate spill formation, infiltration and evaporation were created. These were used to simulate the experimental spills. Comparisons with experimental data ranged from fair to good.

The value of this research effort lies in: the development of equipment and methodologies needed to simulate spills of immiscible liquids; the provision of an experimental data base to help in understanding HIL spills; the creation of mathematical models for rapid simulation of a broad range of possible HIL spill conditions for which experimentation would not be practical.

3.1 Spill Simulation Models

Spill models were developed to aid in understanding how spills of HIL form, move outward and penetrate the soil. They were also designed to assist with spill remediation by providing a rapid simulation of the lateral and vertical spreading of the liquid. In this regard, the work has made an important contribution to the science of HIL spill management, providing the first models of their kind for HIL.

3.1.1 The Wall Model (TR2)

The Wall spill simulation model developed in this research takes account of two specific conditions, (a) discharge from a source onto an inclined soil surface producing a hydraulic bore of spilled material moving down the slope (analogous to border irrigation), and (b) discharge onto a horizontal soil surface creating an enlarging circular pool of spilled liquid.

In both cases, provision is made for variable liquid inflow, infiltration to the soil and evaporation into the atmosphere. The processes which govern spill formation were expressed in the form of the St. Venant Equations with rectangular co-ordinates for condition (a) and polar co-ordinates for condition (b). These equations are nonlinear, nonhomogeneous, first order, hyperbolic partial differential equations. The system accounts for supercritical and subcritical flow, a moving hydraulic jump and a moving bore. Because of the complexity of these equations, analytical solutions were not possible. Several approximate solution methods were examined in detail with the MacCormick explicit finite difference scheme proving to be satisfactory in most cases. The preservation of both mass and momentum and numerical dispersion were checked as solutions were generated by the model.

The spill of a viscous volatile liquid involves the dynamic interaction between forces which drive the liquid over the soil surface (momentum and pressure) and those which resist it (viscous and surface friction). Resistance to overland flow controls the depth, the shape of the spill and the location of the hydraulic jump. Because of the presence of fluid turbulence, resistance to flow in this model was expressed in terms of the Darcy-Weisbach relations with the introduction of a constant friction factor (Kincaid, 1970)*

Infiltration of the liquid during spill formation is a complex system which depends on both capillary and gravity forces. The approach taken in this work was a simplification of the true system. A tubular configuration with both capillary and gravity components was used. Coefficients for the model must be determined experimentally. Evaporation from the pool formed by the spill was represented as a mass transfer equation (Sutton, 1953; MacKay and Matsugu, 1973) adapted for southern Ontario conditions.

Other models have been developed to simulate a liquid spill but these were judged to be insufficient for this work. In most cases the authors failed to account for the energy in the inflow. Many, in fact, used an instantaneous spill with constant depth. Others omitted infiltration and evaporation from the analysis. The need for a more complete model structure was recognized.

The literature review associated with this study failed to locate existing data, from either field or laboratory experiments, for use in verifying this spill simulation model.

* Reference is listed in Technical Report, TR2

Test Simulations

A series of test spill simulations were performed with the model;

- A. to evaluate its overall performance, especially with respect to mass and momentum transport,
- B. to test the sensitivity of spill formation to model input parameters such as rate of inflow, soil roughness and infiltration rate, and,
- C. to examine the spilling of various liquids under a range of conditions.

Two examples of the simulations performed are shown below.

Case 1

Case 1 simulated a slow spill of liquid from a long container, (perhaps a train tank car on its side) onto a sloping soil surface.

- flow $Q = 2.32 \times 10^{-3} \text{ m}^3 \cdot \text{s}^{-1}$ per m of tank width
- soil slope(s) = $7.5 \times 10^{-4} \text{ m.m}^{-1}$
- soil roughness (n) = $3 \times 10^{-2} \text{ m}^{1/6}$
- node spacing = $2 \times 10^{-2} \text{ m}$
- evaporation and infiltration were not considered.

The model used in this analysis was in the rectangular co-ordinates format because of the sloped surface. The output is shown in Figures 1, 2, and 3. Figure 1 shows the location on the liquid front (or moving bore) with respect to time. It must be noted that edge effects have been excluded from the model. Therefore, no lateral spreading of the liquid is accounted for and a rectangular-shaped spill is produced. The simulation becomes a "worst case" in terms of spill length being longer but narrower than the real spill.

Figure 2 shows the fluid profile (depth vs. distance) at 5 time

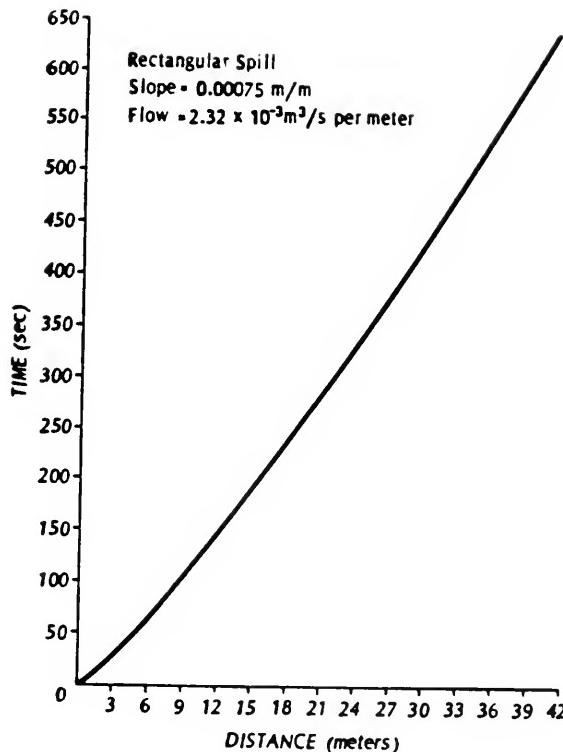


Figure 1 LOCATION OF THE SPILL FRONT WITH TIME

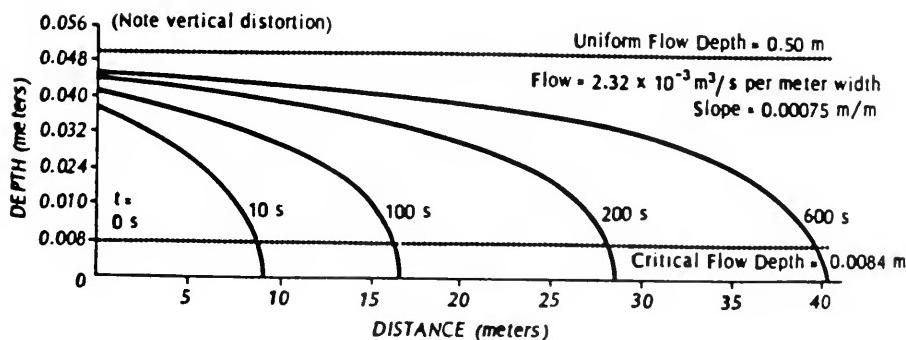


Figure 2 DEPTH PROFILE FOR SPILL WITH TIME

periods up to 600 seconds and compares uniform and critical depths for the flow field (note vertical distortion). Figure 3 shows the velocity profile. It can be seen that, as expected, the spill depth increased with a corresponding reduced velocity as the spill distance increased. Both fluid mass and momentum were preserved. Since subcritical flow existed, no hydraulic jump was produced.

Case 2

Case 2 involved the spill of a liquid onto 3 flat surfaces consisting of asphalt, clay loam and coarse sand. The source of the spill was assumed to be a ruptured container with volume of 62.5 m^3 , a rupture effective diameter of 0.4m and a discharge coefficient of 0.85. The decreasing flow produced from this configuration was $Q = 0.704 - 0.004t$ with t in seconds. A specific rate of infiltration was assigned to each soil (0 for asphalt and >0 for clay and sand). The ponded liquid evaporation rates were the same for each soil.

The model written in polar co-ordinates was used in this simulation to produce a circular pond with time increasing to 326 seconds.

Figure 4 shows the depth (note vertical distortion) profile for the spill on the asphalt surface. The relative locations of the spill front and the hydraulic jump are shown.

Figure 5 shows the location of the spill front and the hydraulic jump for the 3 surfaces with respect to time. The spill front on coarse sand actually retreats somewhat in response to the combined effects of decreasing flow, infiltration and evaporation.

Figure 6 shows the situation for the clay loam by comparing the total spilled volume with the ponded, infiltrated and evaporated volumes. By comparing Figures 5 and 6, it can be seen that the pond

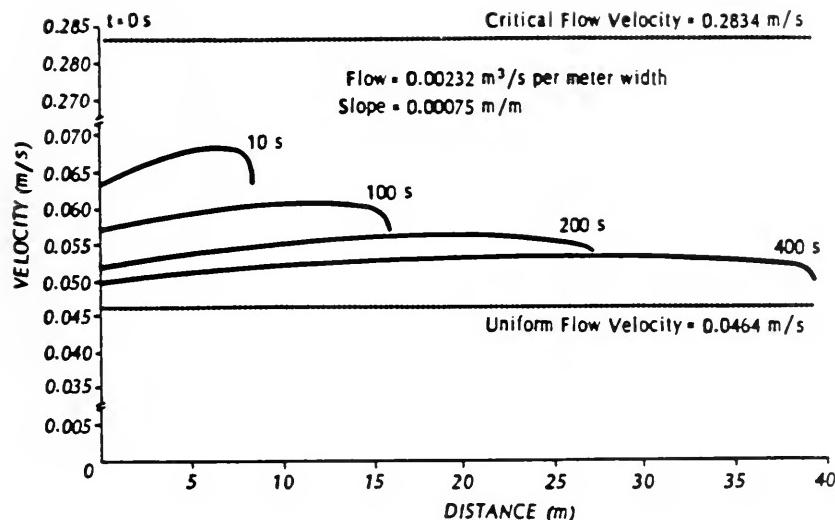


Figure 3 VELOCITY PROFILE FOR SPILL

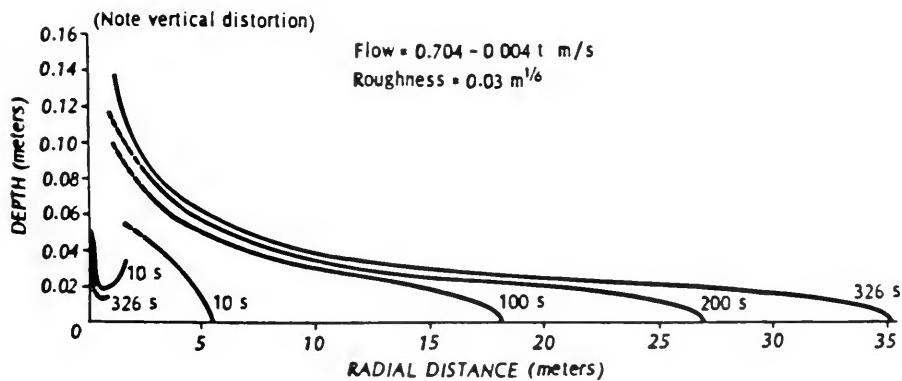


Figure 4 DEPTH PROFILE FOR RADIAL SPILL
ON TO FLAT IMPERVIOUS SURFACE

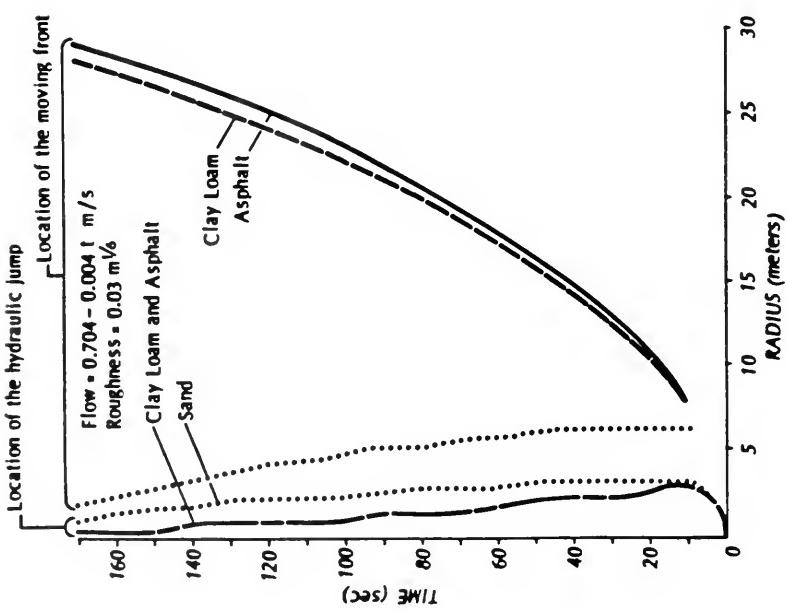


Figure 5 LOCATION OF THE HYDRAULIC JUMP AND MOVING FRONT

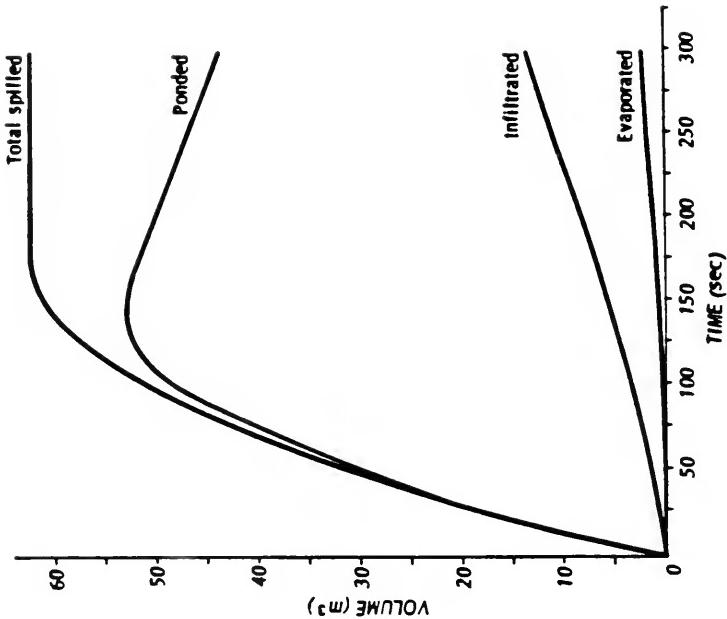


Figure 6 ACCUMULATED VOLUME DISTRIBUTION FOR SPILL ON TO CLAY LOAM

volume decreases although the pond diameter increases.

The results of the model testing indicated that it can produce realistic spill simulations in response to a variety of input conditions while conserving mass and momentum.

3.1.2 The MBPF Model (TR3)

The Wall model was tested against spill data collected in the laboratory and was found to simulate the experimental results reasonably well. However, the model had a deficiency in that the phenomena of fluid viscosity, liquid to solid surface roughness and contact angle and liquid to air surface tension can be handled only in a single parameter, Manning's "n". Unfortunately, Manning's "n" values are available only for water and are also poorly quantified for very rough surfaces such as heavily grassed soils. Consequently, it was considered important to study the modelling process further in order to improve this deficiency. Because of the complexity and therefore the operating cost of the Wall Model, it was decided to explore more simplistic models as an initial step in the study of surface roughness, contact angle and surface tension. The MBPF Model was produced as a result.

After some initial investigation, the equations of Raisbeck and Mohtadi (1974)* developed for petroleum spills onto arctic soils were selected as a basis for this work.

No equations exist to handle the infiltration of HIL into soil. As a substitute, the typical equation used for water (Viessman *et al.*, 1977) was added to the model.

* References are listed in Technical Report TR3

$$F = F_c + (F_o - F_c) e^{-kt}$$

where

F = infiltration rate (m.hr^{-1})

F_o = initial infiltration rate (m.hr^{-1})

F_c = steady state infiltration rate (m.hr^{-1})

t = time (hr)

k = decay coefficient (hr^{-1})

Evaporation was modelled using the equation of MacKay and Matsugu (1973).

Fluid flow in response to a hydraulic gradient as resisted by the solid surface was expressed in terms of Manning's Equation. Unfortunately, the n values required for Manning's Equation have been established for water only. Very little data exist for HIL. The relationship of Rouse (1967) was used to include the influence of viscosity (c) on n .

The surface affinity depth (y_a) (the liquid depth at the bore) was given (Thibodeaux, 1979) by

$$y_a = \sqrt{\frac{2\gamma(1-\cos\theta)}{\rho g}}$$

where:

γ = air: liquid surface tension, (N.m^{-1})

θ = liquid: solid contact angle, (-)

ρ = liquid mass density, (kg.m^{-3})

g = acceleration due to gravity, (m.s^{-1})

The implementation of this equation was an attempt to introduce specific fluid properties to the analysis.

The details of the model are presented in Technical Report TR3. In

summary, the use of the spill simulation model at any time in the spill, involved the following steps:

- A. Estimate approximate spill size using the flow to that time and the y_a value.
- B. Use the area so calculated to estimate the infiltration (F) and evaporation (e) rates.
- C. Using F and e , estimate a new spill volume and size; iterate to a tolerable error.
- D. Calculate the surface profile (using backwater curves).
- E. Compare to measured data.

Since the model and its components are inexact representations of a spill and since data were not available for many of the model coefficients required, the model was fitted to experimental data using n , F_0 and k as fitting coefficients and the bore travel distance and maximum depth as the fitting parameters (i.e. comparative parameters between model and experimental).

3.2 Experiments with Spills of Immiscible Liquids

Experimentation was performed with several objectives in mind; to provide information about the movement and retention of HIL onto and into soil under both laboratory and field conditions, to produce a data base for use in calibrating the models developed in the work, and to develop experimental methods and equipment suitable for the study of HIL and vapour movement in soil.

3.2.1 Preliminary Laboratory Scale Experiments

A laboratory scale (2.4m x 2.4m x 0.15m high) spill simulation box was constructed and tested with water using a declining rate spill. The

spills were video taped and quantified in terms of spill and hydraulic jump radius and fluid depth with respect to time. The purpose of these experiments was to provide the start of a data base on spill behavior with which to understand spills and to evaluate the spill simulation models. Preliminary model runs exhibited excellent agreement with the experimental results for the hydraulic jump and reasonable agreement for the moving front. It appeared that the low surface attraction between the spilled water and the coating on the spill platform surface held back the moving front. Comparative experiments with ethanol, having a much greater ability to wet the surface, produced a moving front which compared extremely well with the theoretical model output.

The first set of experiments involved spilling liquids onto a flat, impervious surface. The radii of the spill and the hydraulic jump and fluid depths were measured with respect to time through the use of video recordings. Experiments made use of a declining rate spill involving liquid volumes up to 5 L and liquid types including water, kerosene and mineral oil. The spill occurred through an orifice with a diameter of 1.0 cm and from a height of 20.0 cm.

The data from one experiment in which 5 L of kerosene were spilled are shown in Figure 7 in terms of spill and hydraulic jump radius with respect to time, the former increasing and the latter decreasing. The simulation of this spill through the use of the Wall Spill Simulation Model is also shown. Excellent agreement between the actual and simulated hydraulic jump locations is evident. However, the model predicted a greater spill radius than was actually measured. The reason for this appears to be related to the interfacial attraction between the fluid and the surface upon which the fluid is spilled. The model

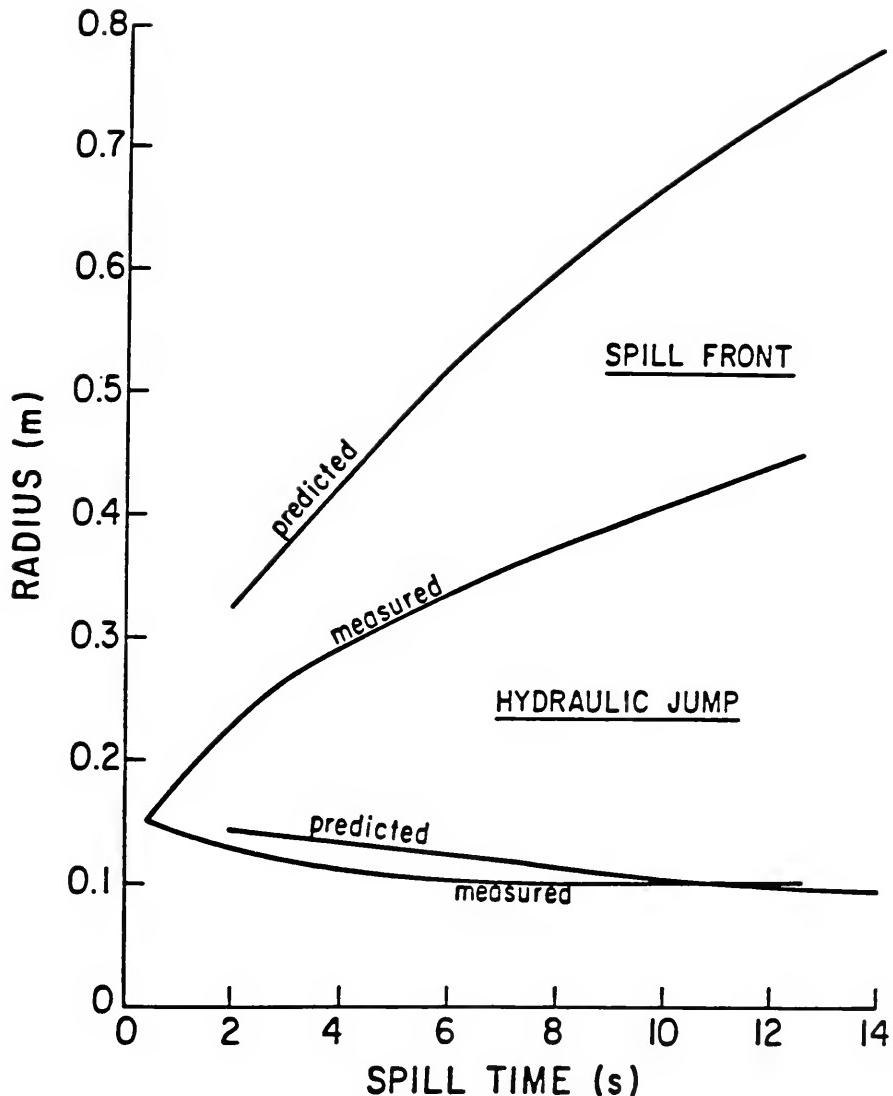


Figure 7 PLOTS OF PREDICTED VERSUS MEASURED HYDRAULIC JUMP AND SPILL FRONT

accounted for most of the important physical properties of the problem - height of spill, declining flow rate, momentum in the fluid, mass conservation, and surface roughness. It did not, however, account for interfacial forces between the fluid and the surface. It was found that, under identical conditions, a spill of kerosene created a larger radius than a spill of water. It was observed that the contact angle between the liquid and the painted flat surface was greater for water than for kerosene and was, therefore, able to support a greater depth of ponded fluid and thus a smaller radius. (The MBPF Model was subsequently developed to overcome this problem).

3.2.2 Detailed Laboratory Scale Experiments (TR3)

Additional spill experiments were performed to examine a wider range of spill conditions to add to the data base available for spills and to evaluate further the spill simulation models. The work was done in conjunction with S.L. Ross Environmental Research Limited, Ottawa. The work was designed to examine infiltration, evaporation, and the effects of liquid viscosity and surface roughness, permeability and slope.

The following range of conditions was examined:

Spill Rate: Constant spill flow rates between 20 and 80 L. min^{-1} were used with the maximum volume spilled in all cases being 200 L.

Surface Treatment: Two surfaces, one impermeable (painted plywood) and one permeable (sodded) were used either flat or sloped at 10° from the horizontal. Sodded surfaces were underlain with a porous mat to permit infiltration and to avoid saturating the sod. Two geometries were used; 2-D as a channel to simulate flow in a ditch and 3-D as a flat surface. These are shown in Figure 8. The

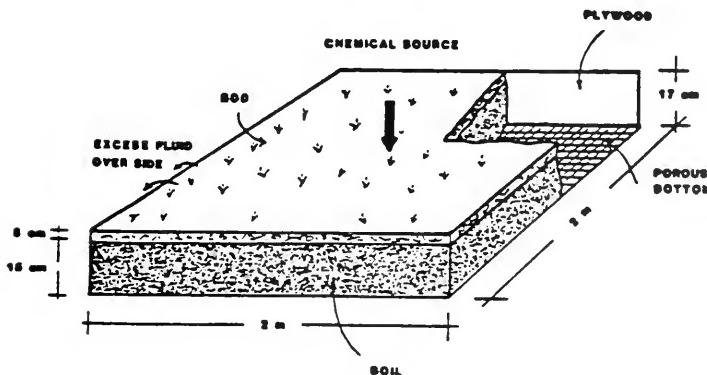
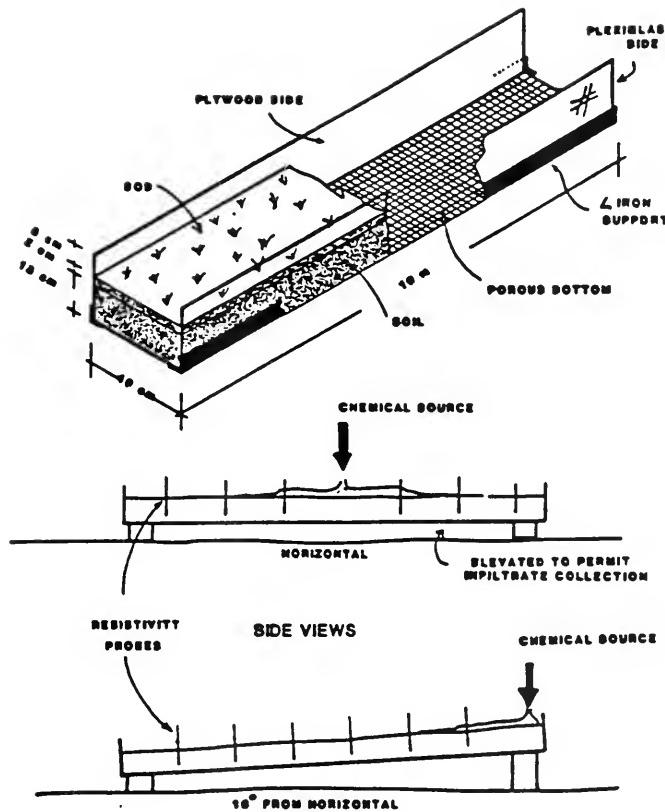


Figure 8 DIMENSIONAL TEST BED

sodded soil was rolled into place and then cores were taken to determine in-place densities and porosities.

Fluid Type: Fluid viscosities (c) ranged from 1 cp to 60 cp achieved by adding increasing amounts of carboxy-methyl-cellulose (CMC) to water.

Detection: The depth of the fluid spills was measured with vertical strips fixed with a wettable paste. The location of the expanding spill front (bore) was detected with the use of resistivity probes at various locations and connected to a multi-channel switching box and then to a microcomputer to log data. Infiltration volumes were detected with a similar set-up. A summary of various spill experiments performed is shown in Table 1.

The experimental results and the model simulations are presented in detail in Technical Report TR3. Some representative information is presented below.

Two Dimensional (2-D) Experiments

The results of 12, 2-D experiments using only water are summarized in Table 2 showing the fitting coefficients of the MBPF Model, Manning's n , initial infiltration (F_0) and decay coefficient (k) and the comparisons between the measured and computed depths. (Note that many experiments were replicated to provide an assessment of the magnitude of the experimental error). Figure 9 shows the actual data collected for Run 1 together with the model simulation.

The comparisons between measured and computed depths are good to excellent on flat surfaces and fair to poor on inclined sodded surfaces. The simulations on sodded surfaces predicted much greater depths than

Table 1 Summary of Run Experiments

Run No.	Fluid Viscosity	Slope	Surface	Flow Rate ($\text{m}^3 \cdot \text{s}^{-1} \cdot \text{m}^{-1}$)
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2-Dimensional

1	water	flat	plywood	0.00046
2	water	flat	plywood	0.0012
3	water	flat	plywood	0.0017
4	water	10°	plywood	0.00140
5	water	10°	plywood	0.00306
6	water	10°	plywood	0.00386
7	water	flat	sod	0.00048
8	water	flat	sod	0.0012
9	water	flat	sod	0.0017
10	water	10°	sod	0.00096
11	water	10°	sod	0.0024
12	water	10°	sod	0.0034
13	c = 15	flat	plywood	0.00038
14	c = 15	flat	plywood	0.00187
15	c = 15	flat	plywood	0.00020
16	c = 46	flat	plywood	0.00032
17	c = 46	flat	plywood	0.0015
18	c = 46	flat	plywood	0.0018
19	c = 65	10°	plywood	0.00061
20	c = 65	10°	plywood	0.0030
21	c = 65	10°	plywood	0.00368
22	c = 5	flat	sod	0.00038
23	c = 5	flat	sod	0.00118
24	c = 5	flat	sod	0.00169
25	c = 15	flat	sod	0.00048
26	c = 15	flat	sod	0.00120
27	c = 15	flat	sod	0.00169

3-Dimensional

28	water	flat	plywood	0.00048
29	water	flat	plywood	0.00108
30	water	flat	plywood	0.0016
31	c = 9	flat	plywood	0.00096
32	c = 9	flat	plywood	0.00107
33	c = 60	flat	plywood	0.00052
34	c = 60	flat	plywood	0.00125
35	c = 60	flat	plywood	0.0018
36	water	flat	sod	0.0011
37	water	flat	sod	0.0016
38	water	flat	sod	0.0021

Table 2 Modelling Results of Water - Two-Dimensional Analyses

Run No.	Slope Condition	Surface Condition	Flow Rate(*) ($\text{m}^3 \cdot \text{s}^{-1} \cdot \text{m}^{-1}$)	Manning Coefficient (best-fit value)	Initial Decay Coeff. ($\text{m} \cdot \text{hr}^{-1}$)	Infiltration Decay Coeff. ($\text{L} \cdot \text{hr}^{-1}$)	Measured	Maximum Depths (mm) Computed
1	flat	plywood	0.00046	0.01	0	0	0	9,8,8,10
2	flat	plywood	0.0012	0.005	0	0	0	10,9,9,5,10
3	flat	plywood	0.0017	0.005	0	0	0	9,12,11,13
4	10° slope	plywood	0.0014(**)	0.015	0	0	0	8,10,9
5	10° slope	plywood	0.0031(**)	0.015	0	0	0	11,10,10
6	10° slope	plywood	0.0039(**)	0.015	0	0	0	11,11,10
7	flat	sod	0.00048	0.75	1.3	0.005	25,25	27
8	flat	sod	0.0012	0.65	2.5	0.005	38,47,37,38	53
9	flat	sod	0.0017	0.65	2.5	0.005	45,41,37,37,33,35	67
10	10° slope	sod	0.00096(**)	0.05	2.5	0.007	25	79
11	10° slope	sod	0.0024(**)	0.05	2.5	0.007	40	177
12	10° slope	sod	0.0034(**)	0.075	2.5	0.007	34	219

Notes - all of the above-indicated results relate to water

- (*) $\text{L} \cdot \text{min}^{-1}$ values from the experiments have been translated to $\text{m}^3 \cdot \text{s}^{-1} \cdot \text{m}^{-1}$. As well, these are flow rates at the location of the spill
- (**) these experiments have flow rates all in one direction, down the slope, as opposed to the experiments on the flat condition which have been presumed to have equal flow in each direction

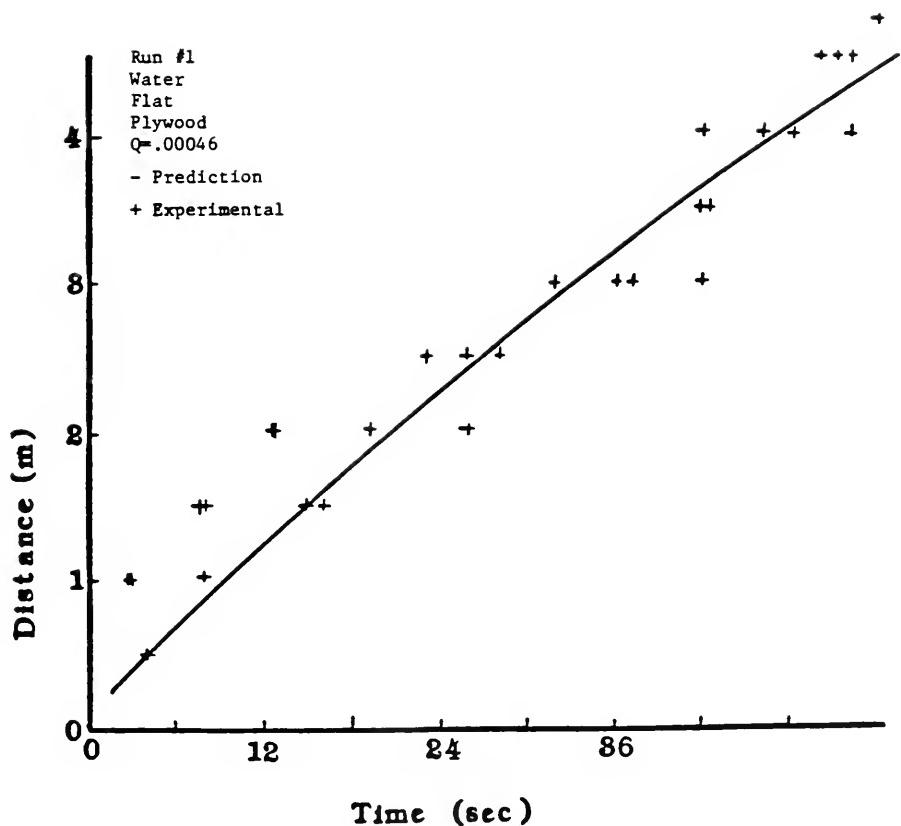


Figure 9 EXAMPLE OF PHYSICAL AND MATHEMATICAL RESULTS FOR PLYWOOD SURFACE

the measured values. This was due in part to under-prediction of the infiltration and to assigning a greater roughness to grass than appeared to be the case since the grass actually bent down during the spill, providing little roughness.

The experimental results obtained exhibited the following trends:

- A. Fitted roughness coefficients (n) were 1 to 2 orders of magnitude greater for the sodded than for the smooth surface. Sloping the surface increased n for the smooth surface but decreased it for the sodded surface.
- B. The maximum spill depths were slightly greater on flat than on sloped surfaces.
- C. Initial infiltration rates were reasonably constant at approximately 2.5 m.hr^{-1} .

The results of a second series of experiments to examine the impact of varying viscosity are shown in Table 3. Again, n , F_0 and k were used as fitting coefficients with comparisons made on predicted vs. measured maximum depths. The model predictions in this case are shown to be extremely good.

The trends in the experimental data include:

- A. Fitted n values were 1 to 2 orders of magnitude greater for the sodded than for the smooth surface. The values tended to be greater for the more viscous fluids.
- B. The more viscous fluids exhibited greater maximum spill depths. Depths were greater on the sodded than on the smooth surface.
- C. The grass on the sodded surface appeared to preferentially adsorb some of the CMC viscosity agent.

An empirical equation by Rouse (1967) relating n to viscosity (c)

Table 3 Impact of Alternative Viscosities - Two-dimensional Analyses

Run No.	Viscosity (C_p)	Slope Condition	Surface Condition	Flow Rate ^(*) ($m^3.s^{-1}.m^{-1}$)	Manning Coefficient (best-fit value)	Initial Decay Coeff. ($m.s^{-1}$)	Infiltration	Maximum Depths (mm) Computed
1	1.0	flat	plywood	0.00046	.01	0	0	9, 8, 10
2	1.0	flat	plywood	0.0012	.005	0	0	10, 9, 5, 10
3	1.0	flat	plywood	0.0017	.005	0	0	9, 12, 11, 13
13	14.7	flat	plywood	0.00038	.10	0	0	17, 18, 18, 19
14	14.7	flat	plywood	0.00187	.065	0	0	22, 22
15	14.7	flat	plywood	0.0020	.05	0	0	22, 24
16	45.8	flat	plywood	0.00032	.15	0	0	21, 21, 22, 22
17	45.8	flat	plywood	0.0015	.10	0	0	17
18	45.8	flat	plywood	0.0018	.09	0	0	31, 30, 30
						0	0	33, 33
4	1	10° slope	plywood	0.00140 (**)	.015	0	0	8, 10, 9
5	1	10° slope	plywood	0.00306 (**)	.015	0	0	11, 10, 10
6	1	10° slope	plywood	0.00386 (**)	.015	0	0	11, 11, 10
19	65	10° slope	plywood	0.00061 (**)	.13	0	0	7, 7
20	65	10° slope	plywood	0.00300 (**)	.06	0	0	6 (+)
21	65	10° slope	plywood	0.00368 (**)	.055	0	0	10 (+)
						0	0	16, 13
7	1	flat	sod	0.00048	.75	1.3	.005	25, 25
8	1	flat	sod	0.0012	.65	2.5	.005	38, 47, 37, 38
9	1	flat	sod	0.0017	.65	2.5	.005	45, 41, 37, 37, 33, 35
22	5	flat	sod	0.00038	1.55	1.25	.003	25, 30
23	5	flat	sod	0.00118	.65	1.25	.003	38, 46, 38, 45
24	5	flat	sod	0.00169	.65	1.25	.003	42, 47
25	15	flat	sod	0.00048	1.75	1.50	.02	35, 35
26	15	flat	sod	0.00120	.65	1.50	.02	45, 47, 40, 45
27	15	flat	sod	0.00169	.65	1.3	.02	55
						1.3	.02	65

Notes - (*) $L.m^{-1}$ values from the experiments have been translated to $m^3.s^{-1}.m^{-1}$

- (**) These experiments have flow rates all in one direction, down the slope, as opposed to the experiments on the flat condition which have been presumed to have equal flow in each direction

- (+) encountered critical flow condition

as well, these are flow rates at the location of the spill

was used in this analysis to evaluate the experimental results. The equation was fitted to the data with good success. The fitting coefficient ranged from 0.91 to 1.5 over 6 pairs of n versus c values with an average of 1.2. It was concluded that the Rouse equation could be used in spill analysis to adjust Manning's n to reflect nonaqueous fluid dynamics.

The experiments involving the sodded surface allowed infiltration of the liquid to occur. The MBPF Model was calibrated using the experimental data and it was found that the F and k values were somewhat higher than those reported for water infiltrating sodded soil. This was attributed to the rather loose packing of the test sod as compared to natural sodded surfaces. It was concluded that the infiltration equation represented the experimental data reasonably well and that it has potential for further use except that experiments with truly immiscible liquids must eventually be done.

Three Dimensional (3-D) Experiments

The 3-D experiments consisted of spilling liquids of varying viscosities onto flat surfaces either smooth or sodded without lateral constraint (as in the 2-D experiments). Measurements of spill depth and diameter were made and used to calibrate the simplified spill model.

Representative results are shown in Figure 10 and Table 4.

The model tended to overpredict the spill diameter (Figure 10) and underpredict the maximum depth (Table 4) although predictions were reasonably good and represented a worst case situation.

The trends in the measured results include:

- A. Spill depths were slightly greater with more viscous fluids and spill diameters were somewhat less.

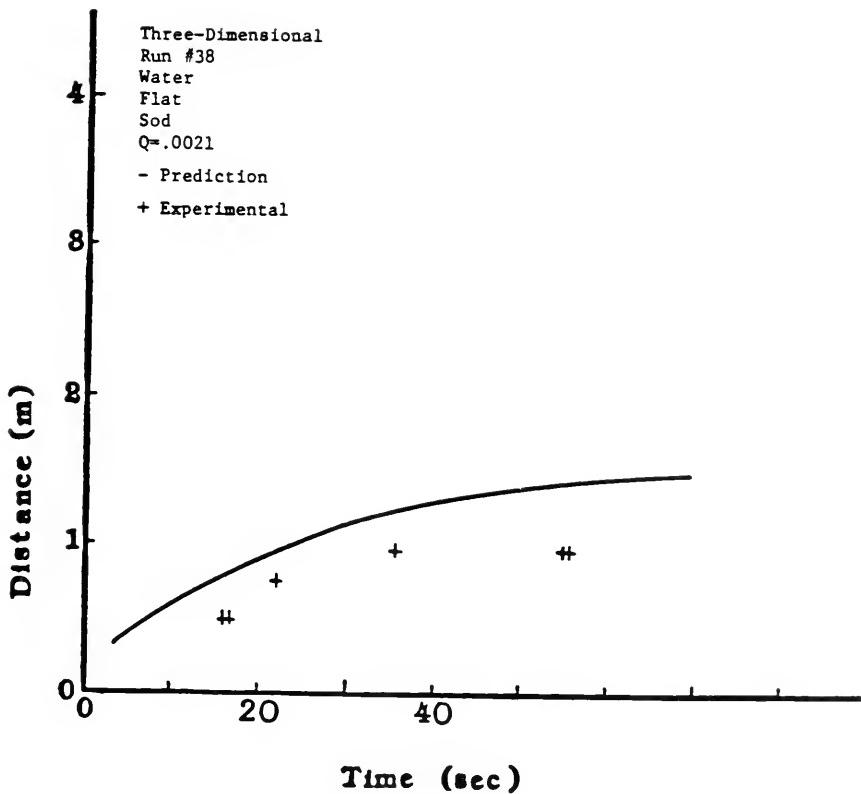


Figure 10 EXAMPLE PREDICTION BY THREE DIMENSIONAL MODEL: SOD

Table 4 Impact of Alternative Viscosities:
Three Dimensional Analyses

Run No.	Viscosity (C_P)	Surface Condition	Flow Rate (L/min)	Infiltration		Maximum Depths (mm)	
				Initial (m/hr)	Decay Coeff. (L/hr)	Measured*	Computed
28	1.0	Plywood	22.04	0	0	6,11,9, 8,7,7, 8,6,6, 6,3,3	3
29	1.0	Plywood	49.25	0	0	7,5,11, 9	5
30	1.0	Plywood	73.1	0	0	8,10,8, 11,8,10, 7,14	6
31	8.98	Plywood	22	0	0	9,9,10, 9	3
32	8.89	Plywood	49	0	0	10,10,11 13	5
33	59.8	Plywood	23.72	0	0	11,13,13,	3
34	59.8	Plywood	56.92	0	0	12,15,14 16	5
35	59.8	Plywood	82.32	0	0	13,23,16 16	7

Notes * Depths taken as the maximum on each surface profile

- B. Spill depths were significantly greater on sodded as compared to smooth surfaces.
- C. The values of F_0 and k were similar to those obtained in the 2-D experiments.

The model was used to conduct a sensitivity analysis of several input parameters. A sample of this is shown in Figure 11 where the impact of infiltration rate on spill size and duration is shown. One important use of a spill propagation model is to allow such analysis to be made. It also then permits the examination of numerous possible spill scenarios impractical to study on an experimental basis.

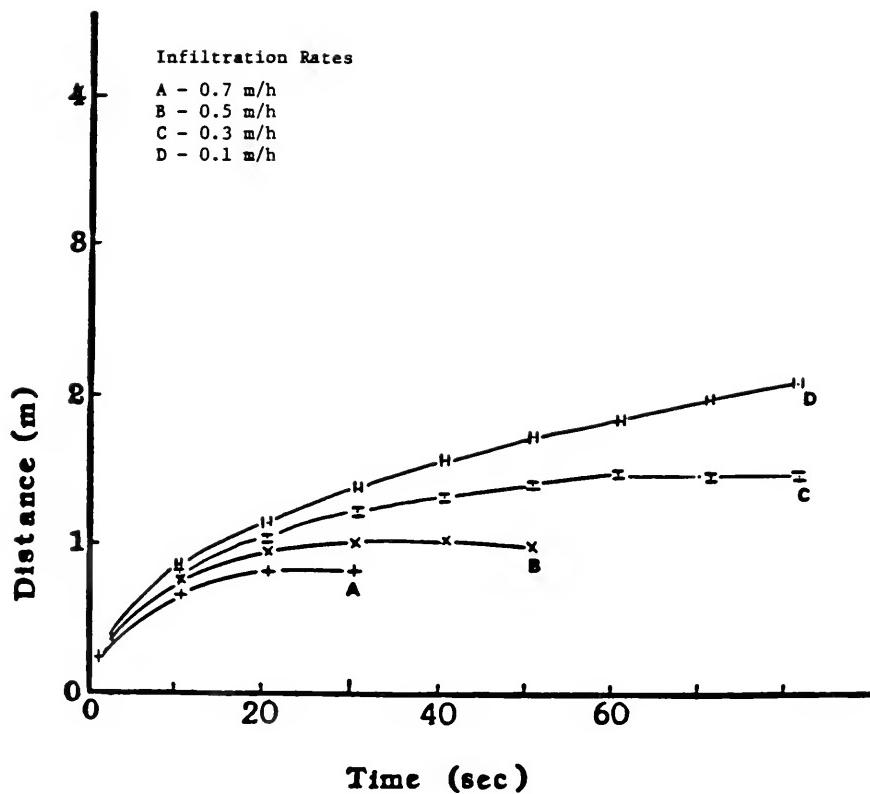


Figure 11 SENSITIVITY OF THREE-DIMENSIONAL MODELLING RESULTS TO ALTERNATIVE INFILTRATION RATES

4. TRANSPORT OF HAZARDOUS LIQUIDS IN HYDROGEOLOGIC ENVIRONMENTS

Immiscible fluids are of environmental concern today because:

- A. the variety and quantity of immiscible liquids have steadily increased,
- B. many of the immiscible liquids are toxic and/or carcinogenic (although only slightly soluble, immiscible liquids are often soluble at concentrations which are above levels considered safe), and
- C. immiscible liquids in soil being poorly soluble remain as a source of contamination for many years.

It is therefore important to understand how HIL migrate through the ground because of the potential danger they pose.

The theory of immiscible displacement was developed and put into practical use in the petroleum industry some time ago to assess the behaviour of oil and gas in reservoirs and to optimize the effects of steam and water-flooding. However, the application of immiscible displacement theory to groundwater contamination situations is a relatively new practice. It is only in recent years that research in this area has taken place. The three major areas of research over this time are worthy of note.

One area of research has involved the movement of hydrocarbons from the surface of the ground to the top of the water table. Hydrocarbons are lighter than water and therefore do not migrate through the water table. Analytical expressions were developed to describe the movement of hydrocarbons in simplified situations and to predict the distribution of water, air, and the hydrocarbon in the ground. Laboratory experiments were performed in sandboxes and columns to examine the

movement of the hydrocarbon front and to get estimates of residual saturations. Papers in this area include work by Van Dam (1967),* Schwille (1967), Mull (1971), Dracros (1978), and Eckberg and Sunada (1984).

Another area of research has examined the migration of hazardous compounds that are heavier than water, most notably the low molecular weight solvents. These immiscible liquids being heavier than water generally sink through the groundwater table. They continue to move down until all the fluid is at residual saturation, until an impermeable layer is reached, or until a layer with an entry pressure greater than the pressure that can be built up by the infiltrating fluid is reached. This research has looked at the migration of compounds in sandboxes and sand columns in different situations. Migration in the saturated and unsaturated zones was examined and the residual saturation of various compounds was investigated. This work was carried out mainly by Schwille ((1967), (1975), (1984)).

The newest area of research is the quantitative evaluation of contamination of groundwater by immiscible liquids. This involves the development of complex finite element or finite difference computer models to predict the movement of immiscible liquids in the ground. The most recent models in the literature include those of Little (1983), Faust (1985), Abriola and Pinder (1985), and Osborne and Sykes (1986). Verification of these models is done by comparing their results to the results of another model or to the 1-D analytical solution of Buckley and Leverett (1942).

* References are listed in Technical Report TR5

In general it must be recognized however, that the body of information available on the transport of HIL in hydrogeologic environments is sparse. As a consequence, the research in this phase of the project was undertaken to assist in this regard. The objectives of the research were to enhance the understanding of data available on HIL movement in soil through experimentation and simulation model testing. The results of this work are summarized below. The details are provided in Technical Reports TR4 and TR5.

4.1 Osborne Model for Immiscible Two Phase Flow in Porous Media (TR4)

The Osborne model for immiscible two phase flow in porous media was developed colaterally with and supported in part by this project.

Mathematical simulation of two-phase flow in porous media has been used in the petroleum industry for some time to analyze the behavior of gas and oil in reservoirs, and to optimize the effects of steam- and water-flooding. Various numerical techniques, including the finite difference and finite element methods have been used to solve the immiscible displacement equations. However, application of such numerical models to immiscible groundwater contamination problems is a relatively new practice.

In this work, a two-dimensional, two-phase mathematical model was developed, based on Darcy's law and conservation of mass for each liquid. The result was a pair of coupled, nonlinear partial differential equations which display both parabolic and hyperbolic characteristics, depending on the magnitude of a nonlinear coefficient.

A numerical model was developed to solve the equations using a

generalized method of weighted residuals in conjunction with the finite element method and linear quadratic isoparametric elements. To alleviate numerical difficulties associated with hyperbolic equations, upstream weighting of the spatial terms in the model was incorporated.

The theoretical and numerical accuracy of the model was verified by comparison with results from an existing one-dimensional finite difference two-phase flow simulator (Little, 1983). This form of verification was necessitated by the lack of actual data on immiscible liquid transport in soil.

One of the comparisons made involved a vertical column of soil 7 m in length and consisting of the 3 soil components shown in Figure 12. The initial distribution of nonaqueous phase liquid (NAPL) is also shown plotted as elevation against % NAPL saturation (S_m) within the zone of saturation. Relationships between relative permeability (k_r), capillary pressure (P_c) and % wetting fluid saturation (S_w) were the same for both models. However, the model developed here was not equipped for hysteretic functions since its intended application was for the first time displacement of water by the immiscible liquid. Thus, only the primary drainage curve was used.

Figure 12 also shows comparisons between the NAPL profiles predicted by the two models. The agreement was thought to be reasonably good and was therefore taken as evidence that the model developed in this work was performing in a satisfactory way.

The finite element model was then used to simulate the migration of an immiscible organic solvent in groundwater, from a chemical waste disposal site located north of Niagara Falls, New York. The effects of uncertainty regarding several of the liquid and porous media properties

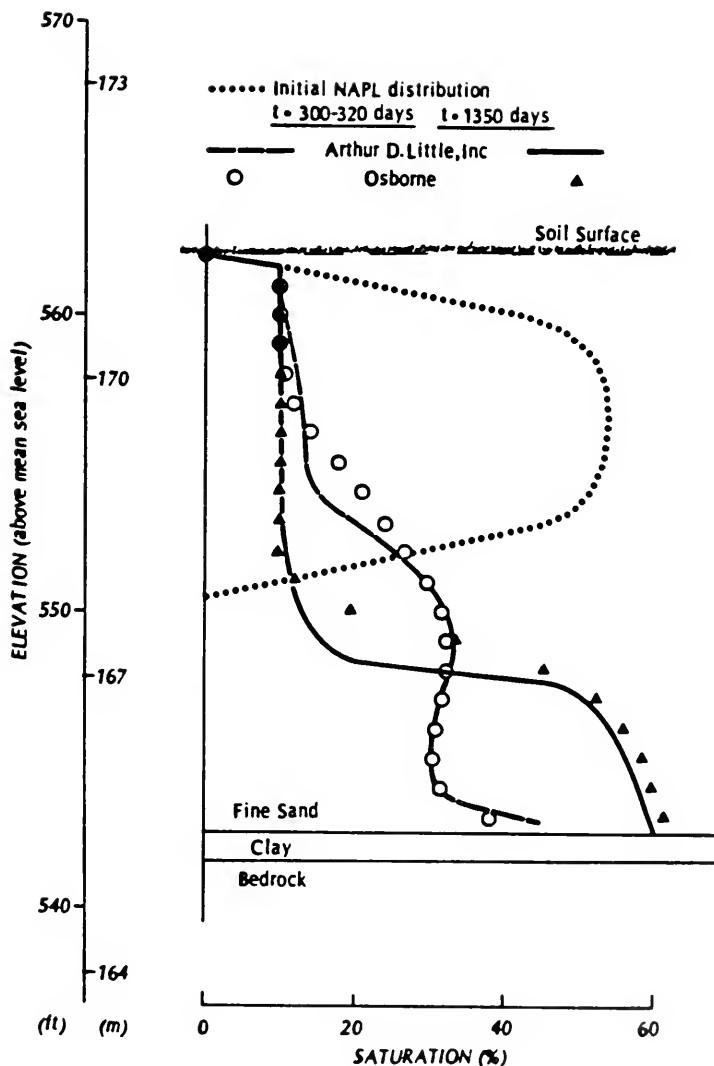


Figure 12 LITHOLOGY AND NAPL SATURATION PROFILES
(Osborne, 1984)

were examined, and it was concluded that the value of the model was limited less by the numerical approximations involved than by the accuracy of input parameter estimations. The results of this simulation are presented in the work of Osborne (TR4).

The model was subsequently used to simulate experiments performed during the project. The results of the effort are dealt with subsequently.

The availability of the Osborne Model is a significant contribution to the solution of HIL spill problems. It can provide useful estimates of how a spilled liquid will behave in the soil; how deeply it will penetrate, how it will behave at the zone of saturation and what will occur if the liquid penetrates the zone. Such information would be most helpful in the design of remedial measures at a spill site and in assessing the severity of a spill/leakage.

4.2 Experiments on Immiscible Liquid Movement in Porous Media

A series of experiments were performed during the project to study and quantify the movement of HIL through soil. These were designed to provide an improved understanding of the processes involved, to serve as a vehicle for equipment and method development and to establish a data base for future work including simulation model testing.

4.2.1 Penetration Experiments

Experiments were performed in laboratory scale columns (7.3 cm diam. x 61.1 cm long) with HIL being allowed to pass through sandy soils under continuous flow conditions. Liquids including oils, hexane, decane and kerosene, were loaded to the columns at various flow rates and antecedent soil water contents. Measurements were made to determine

the rate of movement of the HIL into the soil. Important information on transport velocities as influenced by liquid viscosity, density and contact angle and soil moisture and permeability were obtained. Very little information of this sort was available prior to this work.

4.2.1.1 Detection Methods

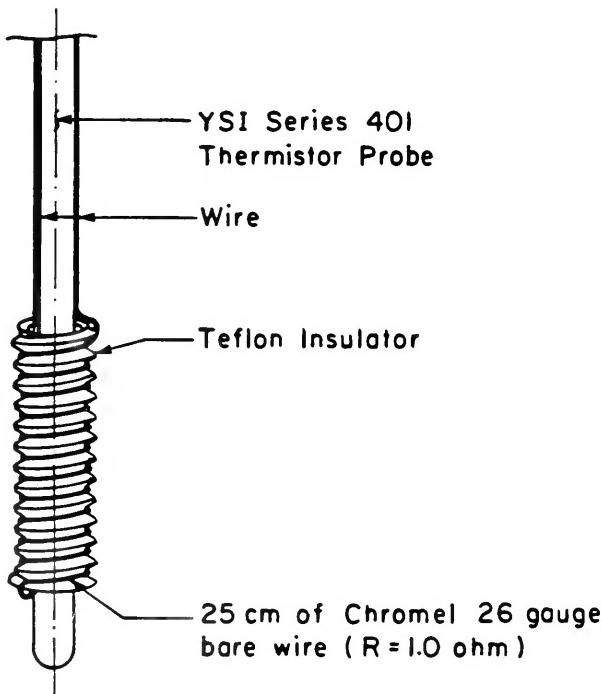
No standard method exists to measure the saturation of two immiscible liquids in a porous media as a function of time and location.

However, a device was developed as part of this work, so as to measure the average saturation of two immiscible liquids over a small area. The device, hereafter referred to as the thermal conductivity (TC) probe, consists of a "thermo" part or coil which pulses a certain amount of heat for a specified period of time and a "probe" part or sensor which measures temperature. Depending on the thermal conductivity of the material(s) between the coil and the sensor, a certain change in the temperature is experienced at the sensor each time a pulse occurs. Since most immiscible liquids of a hazardous nature have a thermal conductivity approximately one-quarter that of water, it was felt that this device could be made to detect changes in the amounts of water and immiscible liquid surrounding the thermoprobe.

The first step in development of the TC probe was to optimize the configuration of the probe so as to obtain the maximum measured temperature change between water and an immiscible liquid for a given pulse of heat. Several designs were tested. They were compared by taking temperature measurements in oil and water and looking at the difference in the measurements (ΔT) for each probe. Based on maximum ΔT , the configuration shown in Figure 13 was considered the best.

The second step in developing the TC probe was to examine the

THERMAL CONDUCTIVITY (TC) PROBE



Scale : Two times actual size

Figure 13 THERMAL CONDUCTIVITY (TC) PROBE

relationship between ΔT and spatial mixture of the immiscible fluids surrounding the probe. It was felt that a linear relationship would exist between ΔT and the % mixture of the immiscible fluids surrounding the thermoprobe. Attempts were made to make homogeneous mixtures of different concentrations of oil and water. The change in temperature could then be measured by the probe for each mixture and a plot of the temperature change per heat pulse versus % oil (or water) made. Mixtures of oil and water were made by using conventional blenders, homogenizers, and by hand mixing in a porous media. However, in each case the oil would start to separate from the water once mixing was stopped. Emulsifiers were then employed to keep the oil and water from separating. Both "Span-80" and "Triton" were used for this purpose with reasonable success as shown in Figure 14. While some scatter in the data are evident, there is clearly a linear relationship between ΔT and percent saturation (% H₂O in mixture). It is also shown that the presence of the emulsifier did not have a major effect on the ΔT response.

The third step in developing the TC probe was to look at factors that might change the reading of the probe other than just the spatial mixture of the immiscible fluids. The factors which were considered were the initial temperature of the fluids, the velocity of the fluids, and the previous wetting history of the soil. The effect of initial temperature of fluid on ΔT was found not to be significant. This was done by taking readings from the probe in water baths at temperatures from 18° C to 40° C. The ΔT readings showed no significant change over this temperature range.

The consequence that different fluid velocities would have on a

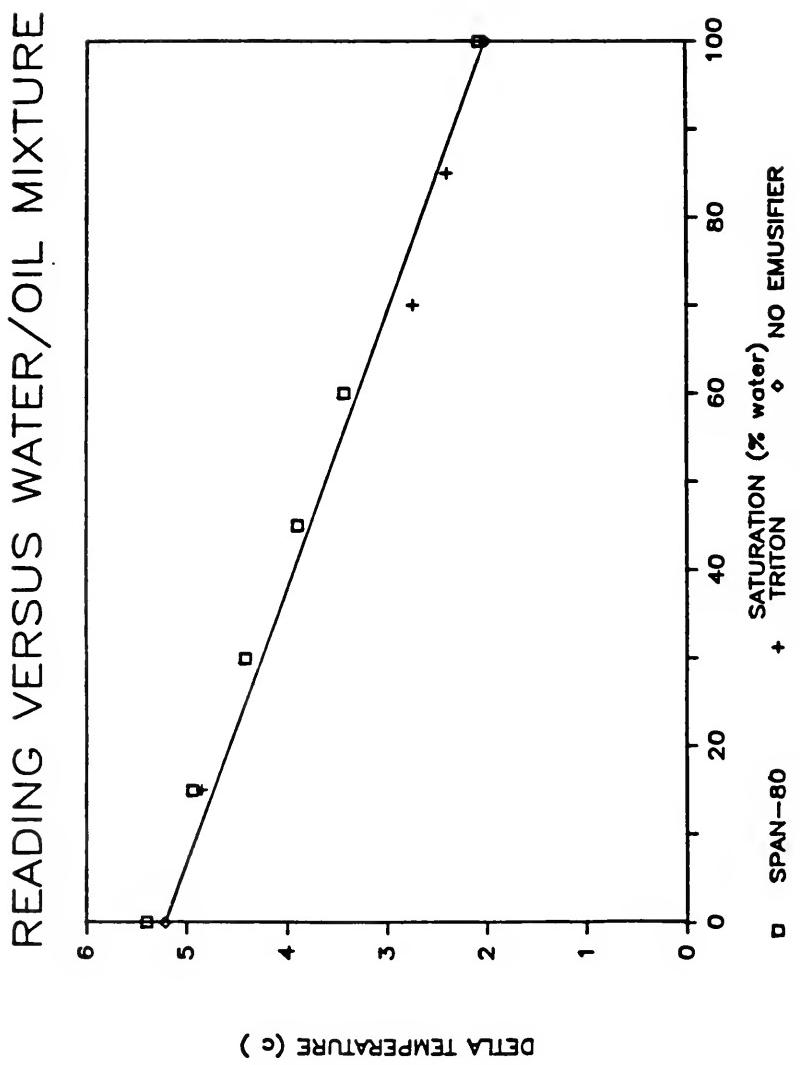


Figure 14 READING VERSUS WATER/OIL MIXTURE

reading was looked at by placing the probe in a column of saturated porous media. Water was passed through the column at various velocities and the probe readings recorded. The results indicate that, at higher velocities in the range of 3.0 cm. min^{-1} or greater, there was a significant effect on ΔT . However, a preliminary correction factor for this error was established. For the range of velocities that was expected with oil flow in soil (up to 0.4 cm. min^{-1}) the effect of velocity on T can be neglected.

The experimentation to assess the impact of previous wetting history on ΔT was conducted by placing the probe first in water, then in oil and then back into water. The readings recorded when the probe was in the water for the second time were initially different from the readings recorded from when the probe was first in the water. However, the second readings gradually approached the first during which time, a visible film of oil appeared on top of the water. Thus, the wetting history did not appear to have a significant effect on ΔT if sufficient time were available between measurements. As well, in a porous media it is unlikely that such rapid changes in the spatial mixture of immiscible liquids as used in this experiment would occur.

4.2.1.2 Example Experimental Results

The results of two experiments are shown in Figures 15, 16 and 17. Figures 15 and 16 show the experimental data recorded as ΔT for the lower and upper TC probe versus time measured from the time of oil entry to the column. Since the thermal conductivity of the oil is less than that of H_2O , ΔT for oil is greater. Relative saturations range from 100% H_2O (0% oil; $\Delta T = 1.25^\circ \text{ C}$) to 0% H_2O (100% oil; $\Delta T \approx 1.85^\circ \text{ C}$). The results show that the oil front was only slightly dispersed with passage

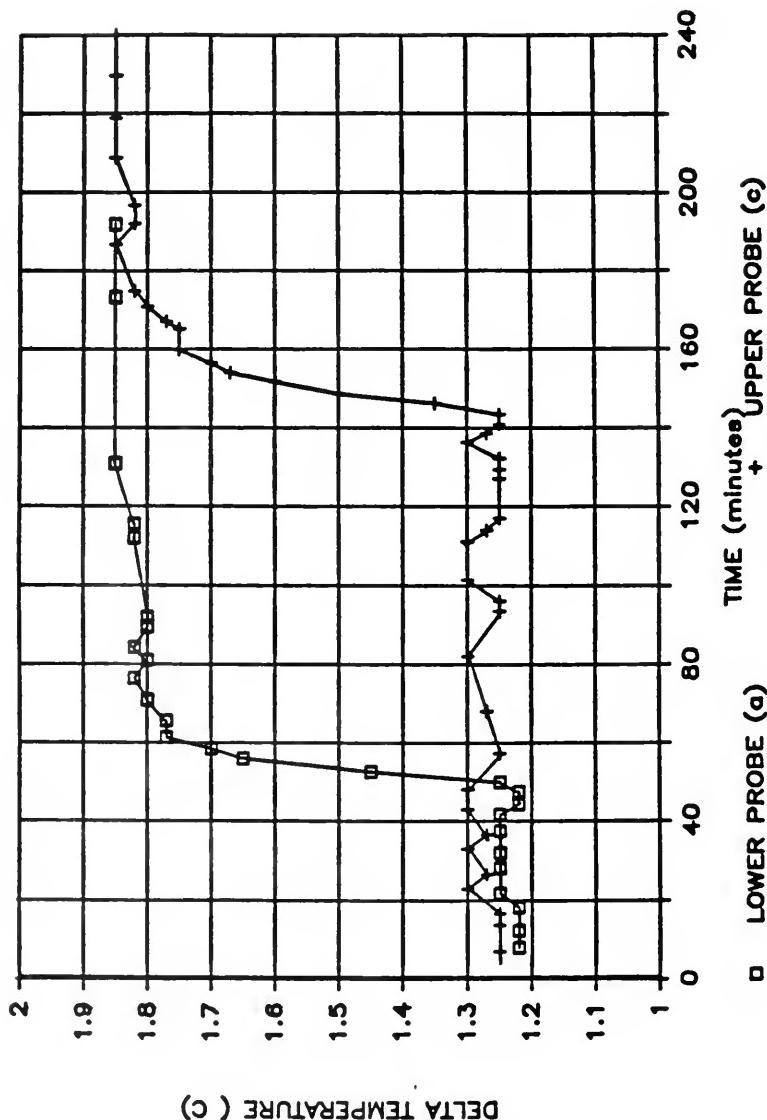


Figure 15 READING VERSUS TIME (EXPERIMENT 2)

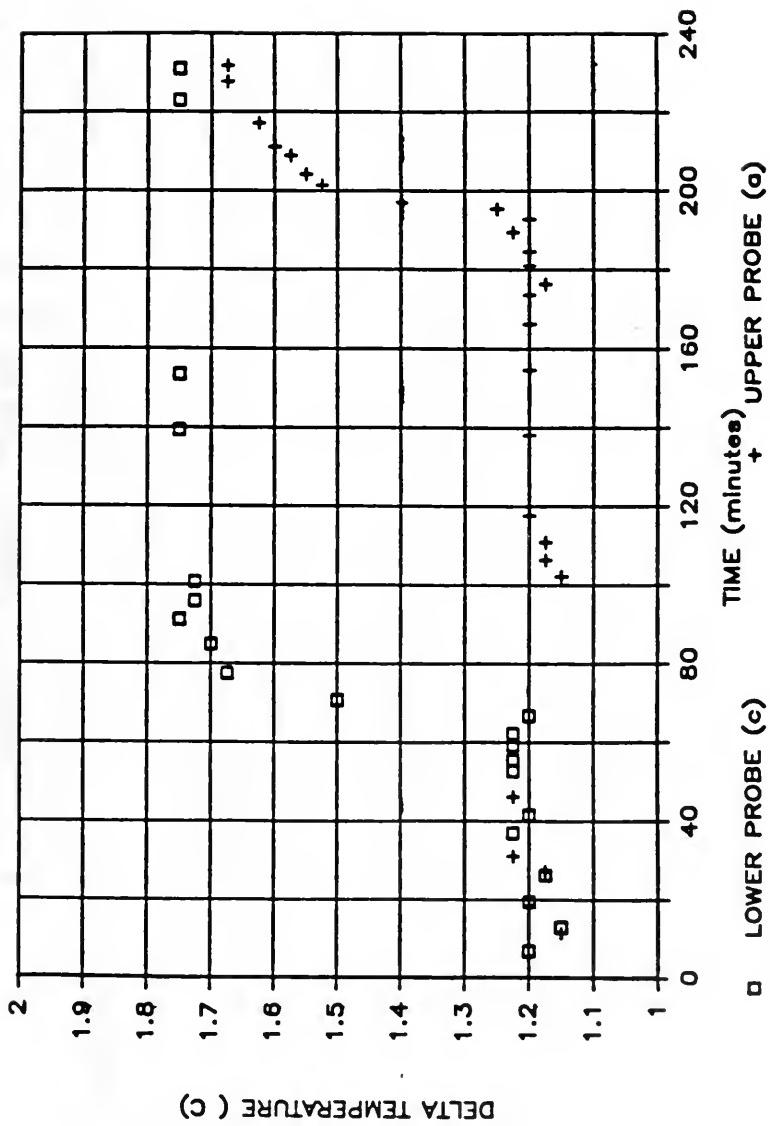


Figure 16 READING VERSUS TIME (EXPERIMENT 3)

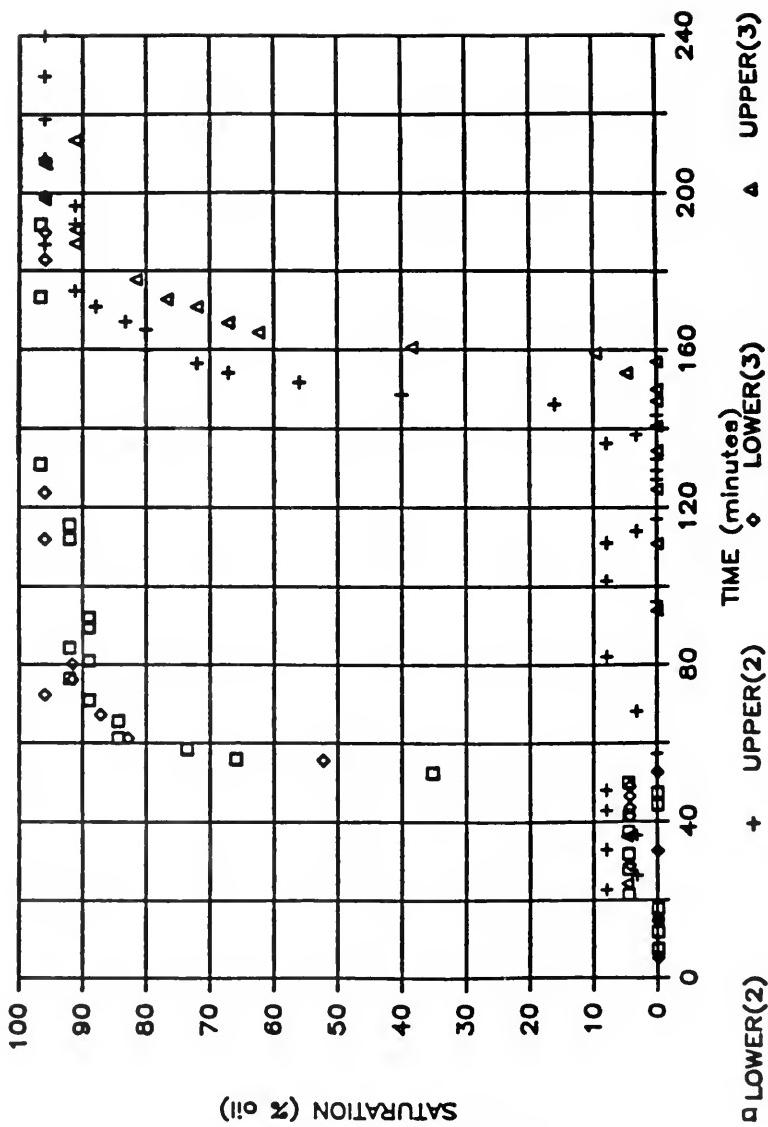


Figure 17 SATURATION VERSUS TIME

from 0 to 100% oil occurring in approximately 20 minutes at the lower probe. The oil used in Experiment 3 was more viscous than for Experiment 2, producing a lower permeability and a slower velocity as shown in a comparison between Figures 15 and 16. The data appear to be very good with only limited scatter.

Figure 17 compares the results from Experiments 2 and 3 by normalizing the data from ΔT values to % oil saturation and by adjusting the time axis from Experiment 3 to that of Experiment 2 because of viscosity differences due to different experimental temperatures. This comparison at the lower probe is excellent with a 10 minute differential shown at the upper probe. The favourable comparisons between the two experiments indicated good TC probe reliability.

The information shown in Figure 18 is in the form of fluid velocity with respect to time for Experiments 2 and 3. As the theory related to the Darcy Equation states, the velocity of the fluid mixture within the column will reduce as the % oil in the column increases. Oil travels more slowly than water and, because of the upflow configuration, the oil regulates the flow. As the height of the oil increases, the hydraulic gradient also reduces. Thus, the first order decay in velocity as shown in Figure 18 is reasonable. Normalized comparisons between Experiments 2 and 3 are excellent.

4.2.2 Measurements of Relative Permeability and Capillary Pressure vs. Relative Saturation

Relationships between relative permeability and capillary pressure versus relative saturation are essential to quantify movement of multiphase fluid systems in soil. As identified previously, limited

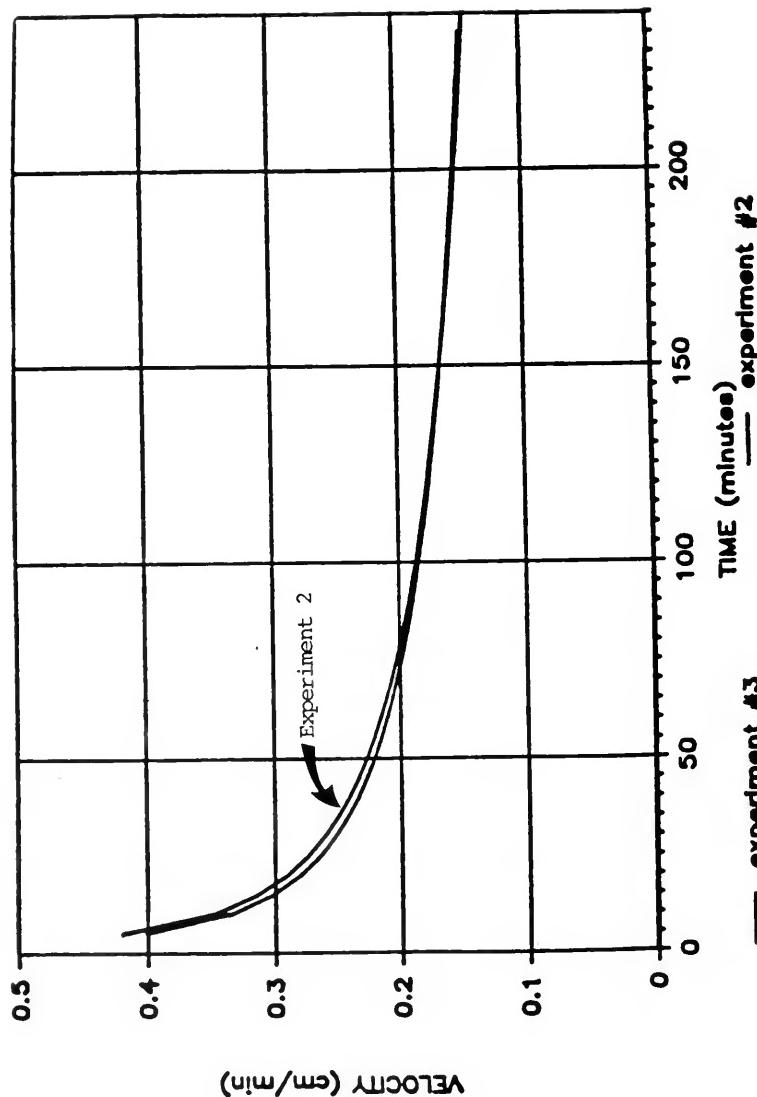


Figure 18 VELOCITY VERSUS TIME

experimentation of this nature has been done for oil-water mixtures but very little for other immiscible liquids. Consequently, this experimental series was designed to fill this need by developing improved experimental methods and then applying them to liquids other than oil.

The experimental method involved use of the standard column of this research to which varying proportions of oil and H₂O were added at constant flow rates. Steady state was defined as the point at which the oil-H₂O proportions of the effluent became steady. The combined discharge velocities and the applied pressure heads were used to calculate the relative permeabilities. The results of the first experiment performed are shown in Figure 19.

Although the results are preliminary, they have the proper form and thus confirm the utility of the method chosen. It must be noted that these experiments are non destructive because of the use of the TC probe. All prior experiments have required that, for each pair of points on the curve, the column be taken apart and the relative saturation be determined using a separate experiment. The continuous flow, non-destructive method developed here is thus a great improvement in methodology. It was subsequently applied to other immiscible liquids in this work.

The results of preliminary experiments to quantify capillary pressure versus % water saturation for drainage conditions are shown in Figure 20. In this case water is the wetting fluid and oil is the non-wetting fluid. It too, has the proper form. Subsequent work was done to evaluate mathematical relationships to predict relative permeability from capillary pressure data. Reasonable success was achieved with this

RELATIVE PERMEABILITY CURVE

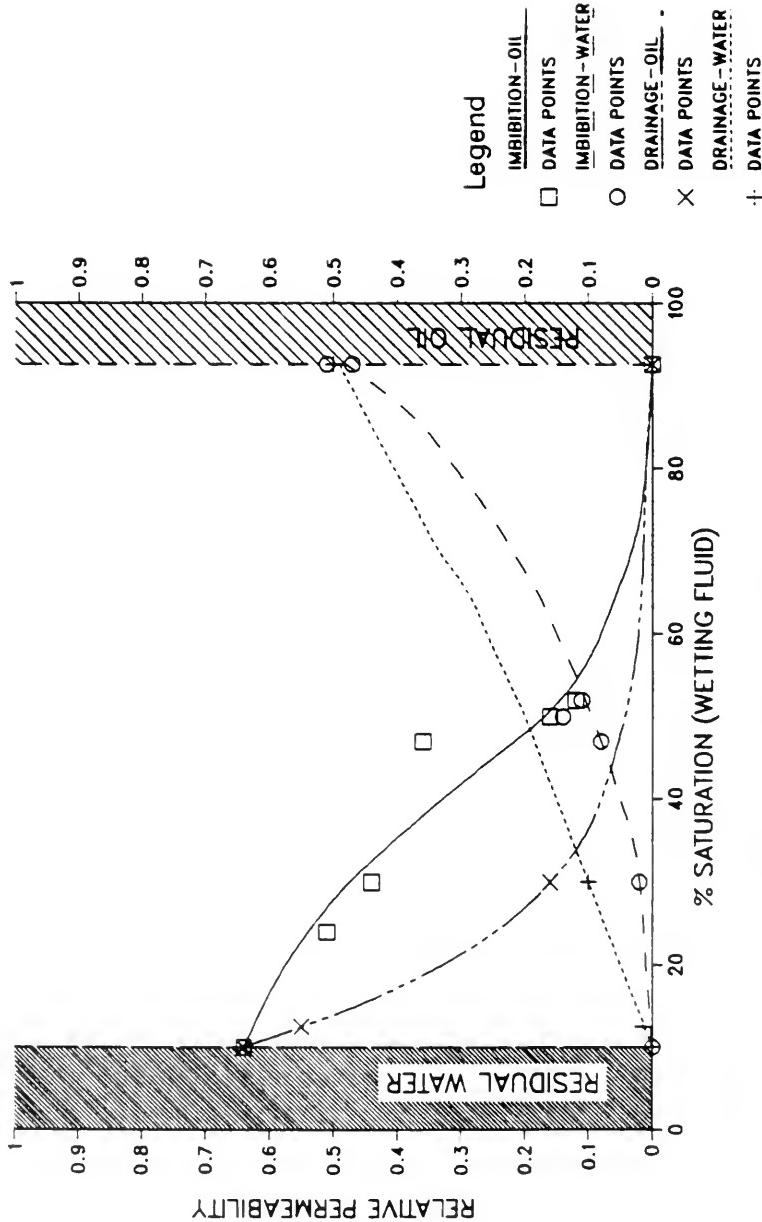


Figure 19 RELATIVE PERMEABILITY CURVE

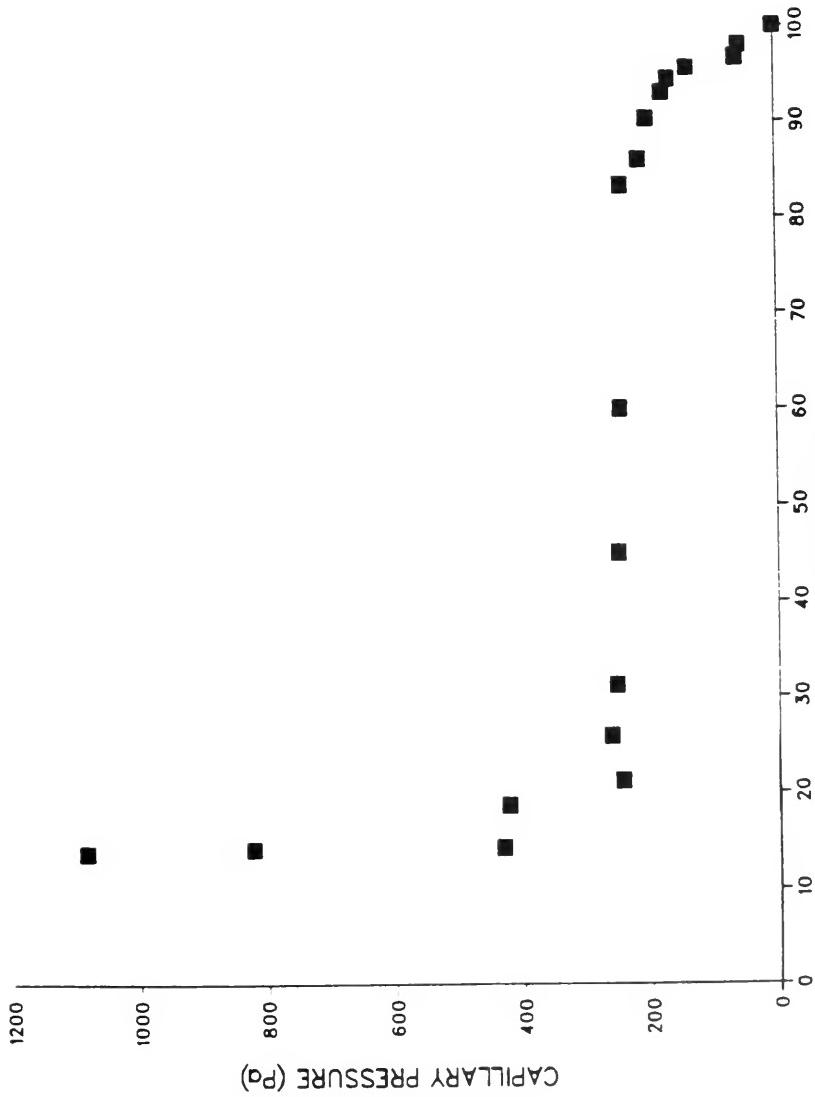


Figure 20 CAPILLARY PRESSURE CURVE DRAINAGE CONDITIONS

method.

4.2.3 Evaluation of the Osborne Model by Comparison with Experimental Data

Two immiscible liquid displacement models were examined to evaluate their suitability for simulating the experimental results of this research. One was the two dimensional, finite element numerical model (WSTIF) produced by Osborne and Sykes (1986). This model makes use of capillary pressure and relative permeability curves as produced in this work. The other suggested by McWhorter (1986), was a one dimensional analytical model using the capillary pressure curve as a step function.

The model simulations ranged from good to fair and appeared to be influenced significantly by the quality of the capillary pressure curve in the region of the bubbling pressure. In general, the numerical model performed better than the analytical one. An example of the simulations is shown in Figure 21. The experiment consisted of the upward displacement of water by oil in the sandy silt soil. The agreement between the numerical model (WSTIF) simulation and the experimental data is reasonably good considering that the model was not fitted to the data. Rather, the model was run independently using input data such as capillary pressure, relative permeability and boundary condition data as collected in the experiments. The results of the simulation study were encouraging because they showed that the numerical model of Osborne and Sykes provides reasonable simulations of real systems. The model appears to have potential for use in field situations where estimates of immiscible liquid transport are required.

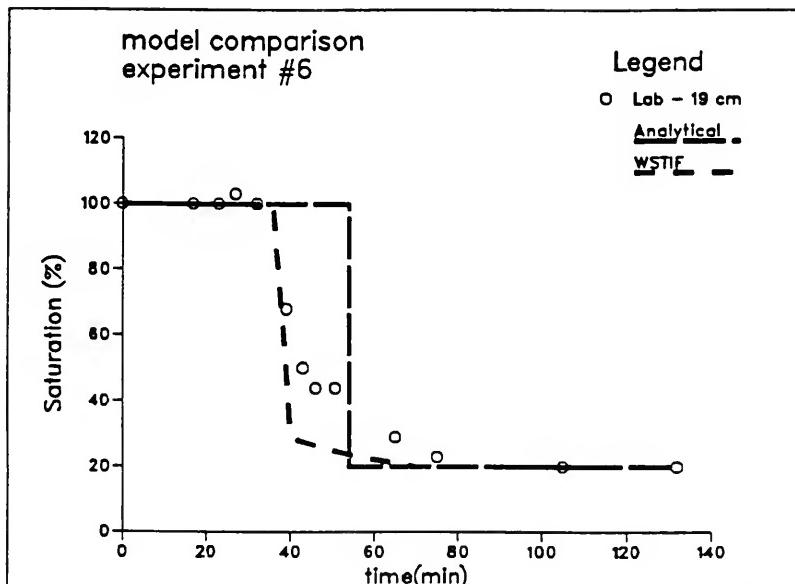


Figure 21 MODELLING RESULTS FOR EXPERIMENT #6

5. MOVEMENT OF HAZARDOUS VAPOURS IN SOIL

Spills and underground leaks of volatile immiscible liquids represent serious health hazards, important components of which are the release and spread of toxic and flammable vapours. There is a scarcity of quantitative data available to assist in the evaluation and remediation of problems involving hazardous vapours in soil. Consequently, research was undertaken in this project to study volatilization and subsequent vapour migration from immiscible liquids in soil and to create a comprehensive mathematical model to describe these processes.

5.1 Allan Model to Simulate Vapour Movement in Soil

The Allan model was developed in this project to simulate the movement of vapours away from HIL retained in soil. The work was based on the methane migration model prepared previously by Metcalfe (1982)*. The model is comprised of partial differential equations for intergranular flow and continuity in porous media (Bear, 1970). The flow is predicted by the Darcy Equation. Estimates of gas conductivity in variably saturated soil are used. The continuity equations account for dispersion, convection and loss terms. Gas diffusion in porous media, dispersion, dissolving from gas into liquid phase and density differences between gases are all taken into account. Discharge of gases at the soil surface is simulated using transport equations for a laminar sub-layer (Thibodeaux, 1979). The model solves a 2-D form of the equations by a numerical, finite element method. It is capable of

* References are listed in Technical Report TR6

operation with a variety of boundary conditions: at the spill, at the soil surface, at depth and at various distances away from the vapour sources; soil structures, properties, and types within the migration zone; liquid and vapour properties; pressure and/or diffusional flow conditions.

5.1.1 Model Simulation of Field Data

The model was used to simulate actual field cases of gas and vapour migration in soil. Since no data were found on vapours arising from hazardous liquids, comparisons were made with the migration of methane gas (CH_4) from a landfill. Field data from the Mississauga landfill were used in this case (Metcalfe, 1982).

The hydrogeologic conditions of the site are shown in Figure 22. Because the simulation started in September and continued into the winter, the first half of the simulation had a radiation-type boundary, open at the ground surface, while the second half had an impermeable ground surface due to a frozen cover.

The results of the model simulation are shown in the concentration contours of Figures 23 and 24. The effect of the changing ground surface boundary can be seen in the contours. During the "open months", the atmosphere acted as a sink and slowed gas transport. The concentrations at the ground surface were very small. In the "closed months", gas movement was more pronounced because the closed boundary allowed gas to build up at the surface and then forced it to move outward from the landfill. The simulated contours closely approximated the actual field measurements (Metcalfe, 1982), as seen in Figure 24. The results show that the model can be used successfully to simulate gas

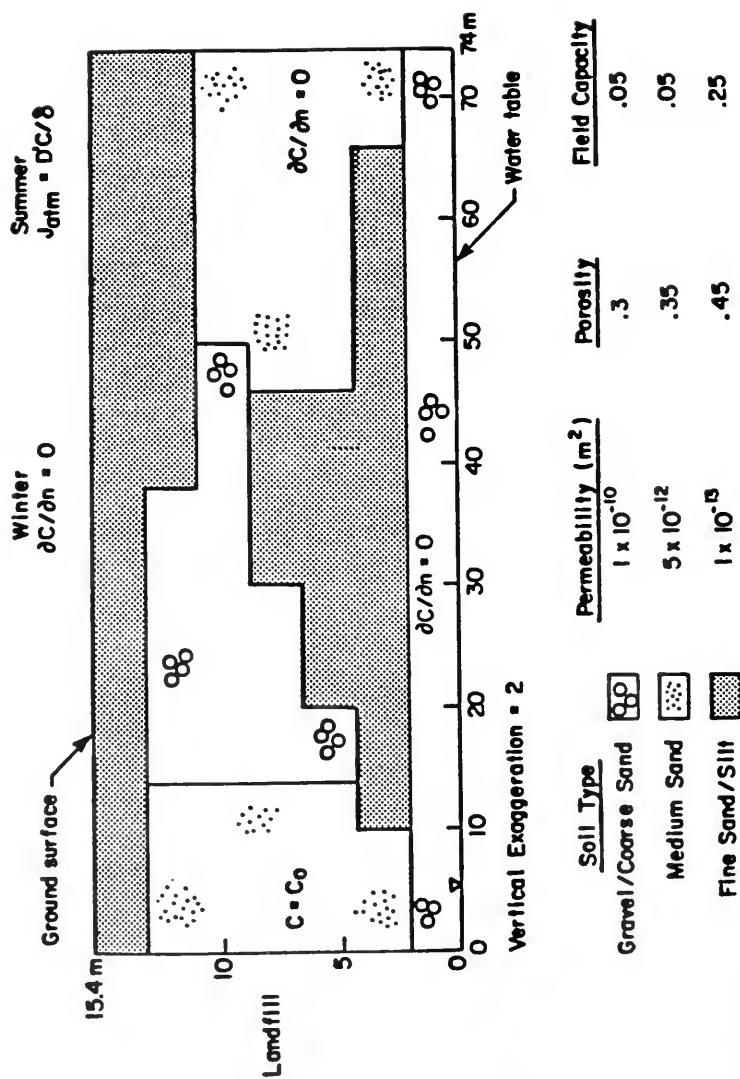


Figure 22 TYPICAL SOIL DOMAIN FOR MODELLING VAPOUR TRANSPORT

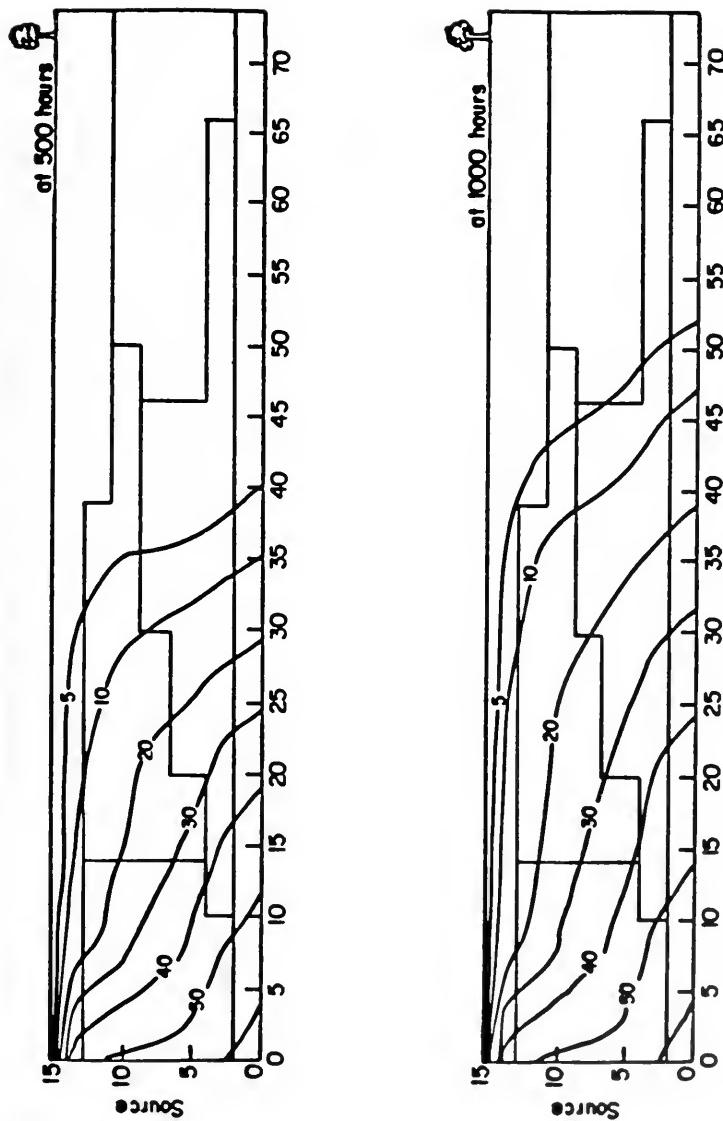


Figure 23 SIMULATED METHANE CONCENTRATIONS (% BY VOLUME) IN SOIL MIGRATING FROM THE MISSISSAUGA LANDFILL; OPEN TO THE ATMOSPHERE

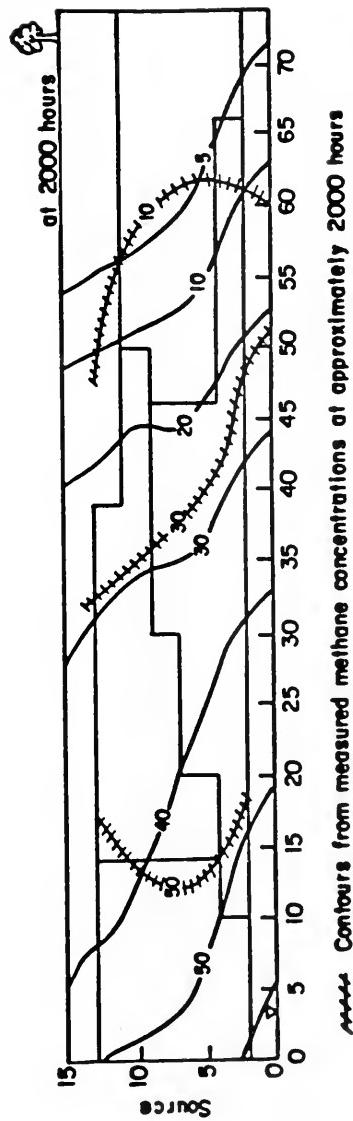


Figure 24 SIMULATED METHANE CONCENTRATIONS (% BY VOLUME) IN SOIL MIGRATING FROM THE MISSISSAUGA LANDFILL; CLOSED TO THE ATMOSPHERE

movement in the field. It was concluded that model was also likely to provide successful simulations of HIL vapours in field situations involving spills and leaks.

5.1.2 Simulation of Possible Cases

One import feature of a simulation model is its ability to explore, at reasonable cost, large numbers of situations which might occur in actual situations. The Allan model was used to demonstrate this feature. One example is shown here. The liquid used was benzene because of its widespread use in industry and the availability of data on its vapour properties (Environment Canada, 1984). Benzene is lighter than, and immiscible in water. Therefore, when a volume of benzene liquid reaches a water table, it tends to spread out or to 'pancake' on the water table. As it rests within the capillary fringe, it releases vapours which will migrate through the surrounding soil. It was this vapour movement that was simulated.

The Dirichlet source is shown in Figure 25. It was assumed that the benzene solution was at saturation with a vapour pressure of 0.1 atmospheres. With a system pressure of 1 atmosphere, a mole fraction of 0.1 is obtained for the Dirichlet nodes. A slight pressure gradient of 0.4 Pa.m^{-1} was imposed on the soil section.

The simulation was run for periods up to 300 hours with concentration contours for 100, 200 and 300 hours shown in Figure 25. The open ground surface boundary prevented any significant concentration buildup near the top of the domain. Because of the high permeability of the lower layer, the benzene plume moves most rapidly in this layer. As well, a small pressure gradient in the x direction can greatly affect the rate of movement of a vapour in soil.

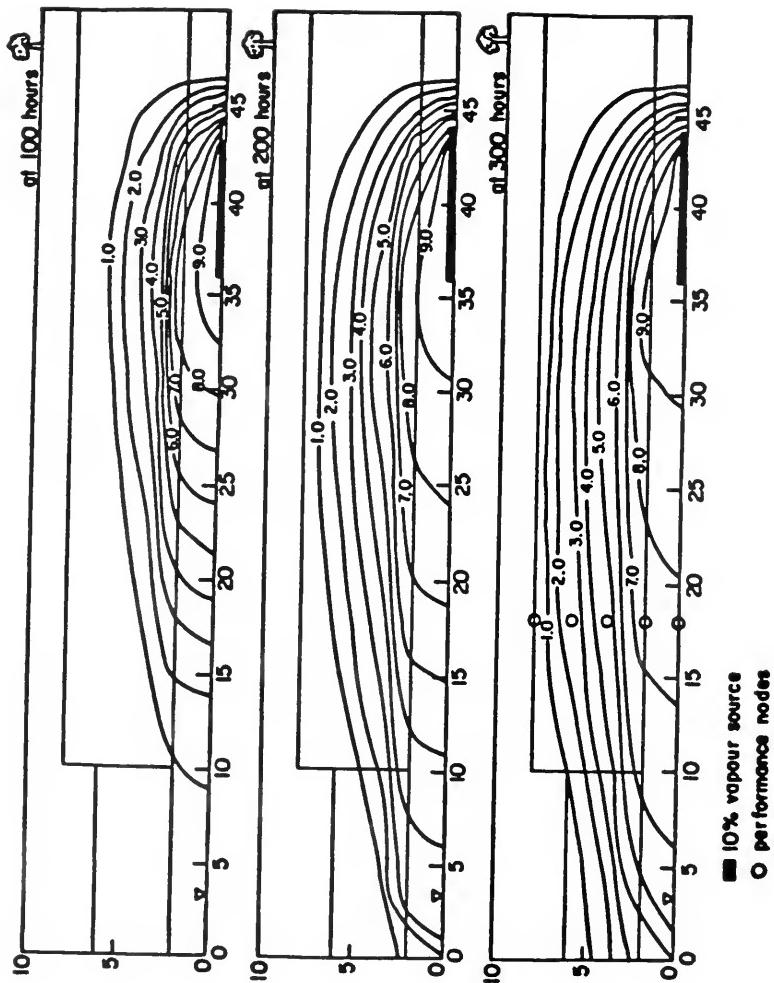


Figure 25 SIMULATION OF BENZENE VAPOUR MIGRATION FROM A PANCAKE SOURCE RESTING ON THE GROUND WATER TABLE

5.2 Experiments on Vapour Movement in Soil

A portion of the project was committed to experiments on the movement of vapours in soil. As with previous experimentation, the objectives were to develop appropriate equipment and methodology, to use these for the study of vapour transport patterns in soil, and to provide a data base for testing simulation models. The work was done on two levels, one with 1-D soil columns and the other with a 2-D rectangular flux box. Sandy soils were used in most cases. Vapours and liquids included methane, hexane, heptane, benzene and acetone.

5.2.1 Soil Column Experiments

Plexiglass cylinders containing a fine silica sand core 7 cm in diameter by 36 cm high, were used to study the movement of gases and vapours in soil. The ends of the column were closed except for two ports for introduction of gas/vapour and for pressure control. An open volume approximately 5 cm high was maintained at the top (head space) and at the bottom (foot space) of the column. A gas contaminant was introduced into either end of the column, depending upon experimental protocol. A small airflow was usually introduced at the opposite end to insure that no contaminant was allowed to build up when maintaining a zero concentration boundary condition at the non-source end. The ports were used to control pressure in the head and foot spaces. Sampling ports were located at 7.5, 15.0, 22.5 and 30.0 cm from the contaminant source. Sampling methods involved small syringes to draw quantities of gas for analysis in a gas chromatograph. Gas concentrations in the head and foot spaces were sampled through the pressure port.

5.2.1.1 Column Experiments with Methane

A number of experiments on the diffusion of methane through porous media were carried out with the soil columns. Figure 26 presents the results of one experiment showing the methane concentrations with time at the four sampling ports in the column. In this case, gas was introduced into the head space, where the concentration stabilized at 87.6 percent for the duration of the experiment. From the figure, it is observed that the gas concentration rate of change and the eventual stable concentration level is inversely proportional to the port distance from the source. In fact, 75 minutes into the experiment, the column concentrations stabilized at what appears to be a linear concentration gradient from the head space (at 86% methane) to the foot space (at 0% methane).

A replication of the experiment is presented in Figure 27. The curves presented are those of Figure 26, while the symbols are data from the second experiment. The precision of the experimental equipment and methods are quite good.

Figure 28 provides a comparison between the column experimental data (curves) and a simulation (points) generated using the Allan vapour transport model. The comparison is extremely good and indicates that the model is an accurate and useful means of providing simulations.

5.2.1.2 Column Experiments with Acetone

The results of a column experiment with acetone are presented in Figure 29. The "y" axis data are presented as a percent of the mean head space concentration (treated as 100%). For this reason, small anomalies such as head space concentrations of greater than 100% were possible. This normalization was necessary because an acetone standard

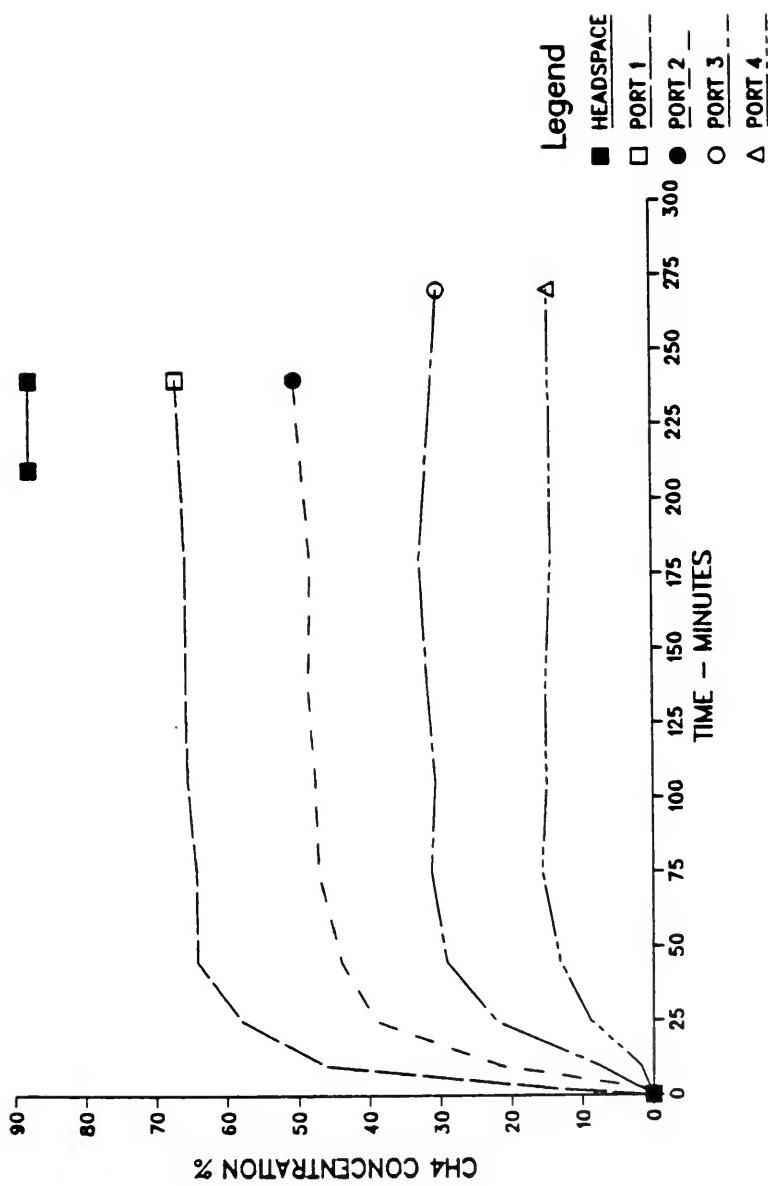


Figure 26 CH₄ MIGRATION IN COLUMN EXPERIMENT 3

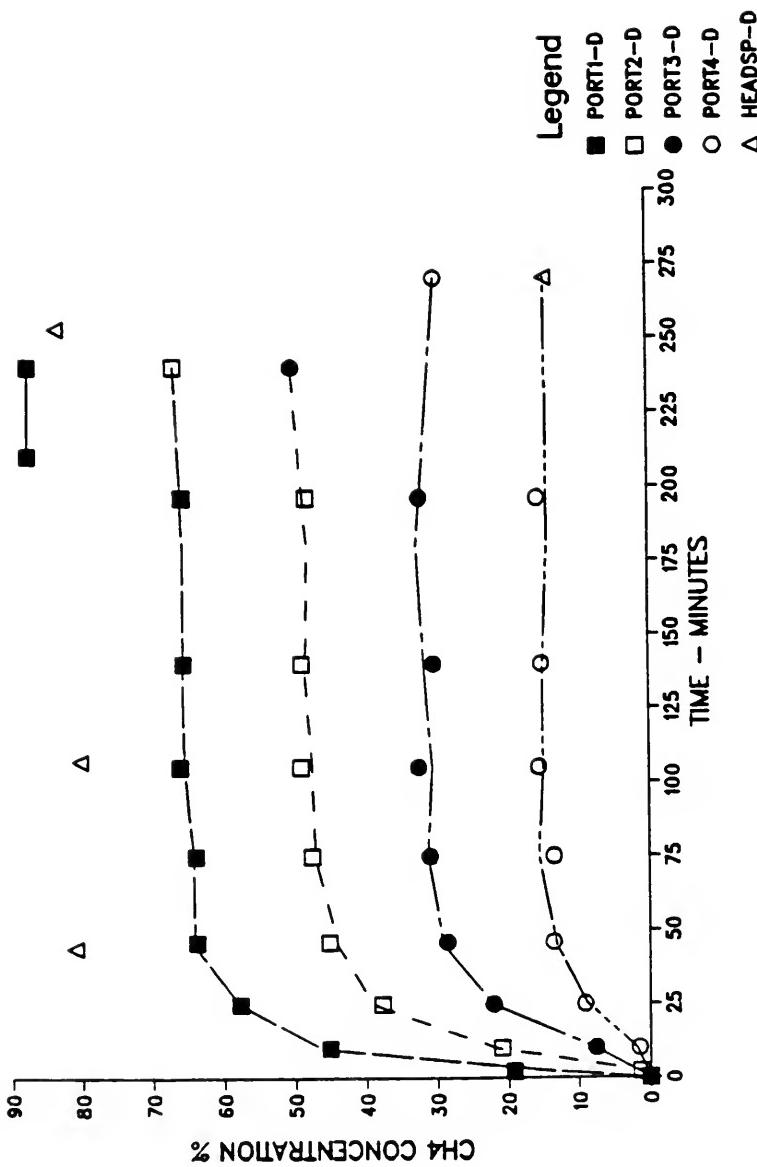


Figure 27 CH₄ MIGRATION - EXPERIMENT 3 REPLICATION

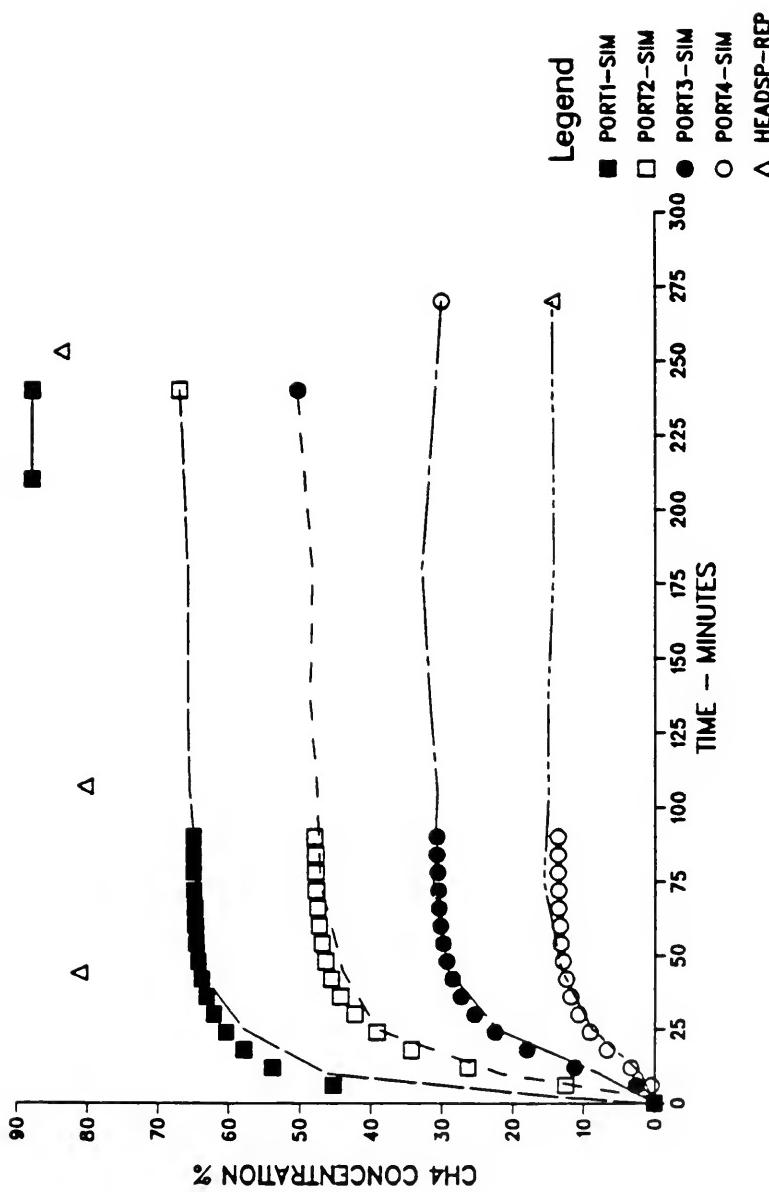


Figure 28 CH₄ MIGRATION - EXPERIMENT 3 SIMULATION

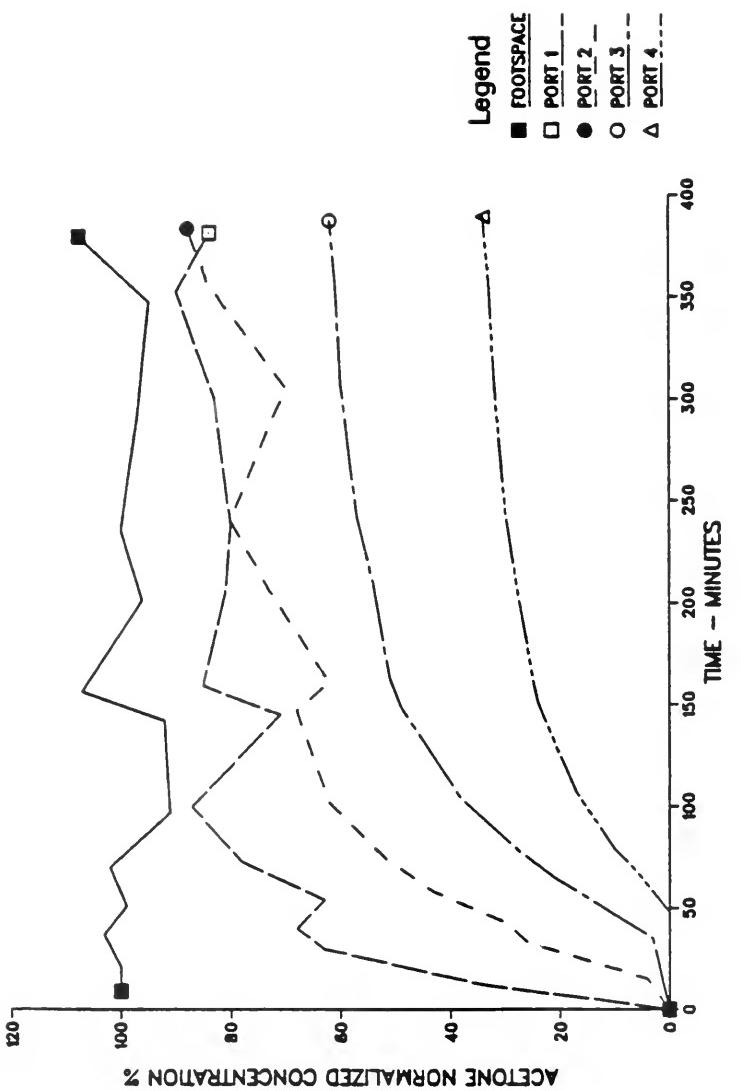


Figure 29 ACETONE MIGRATION IN COLUMN EXPERIMENT 3

was not available when the experiment was run.

The results are quite similar to those obtained with methane. The acetone curves exhibit a lag due probably to the use of a liquid as opposed to a gaseous source as for methane. The formation of an equilibrium vapour phase acetone concentration would take some time. The variability at ports 1 and 2 (nearest to the source) is also assumed to have been due to variations in vapour formation at the liquid source.

No model simulations were done for this experiment. Several other experiments were performed to test methods and equipment and to examine other vapours with similar results.

5.2.2 2-D Flux Box Experiments

The flux box (3.6 m long x 1.2 m high x 0.3 m wide) was designed for larger scale vapour transport experiments in soil. Source liquids can be introduced along the base of the box or within the soil at various points. Ports for sample extraction by syringe and pressure measurement exist along the sides of the box. The soil surface can be open or sealed, vegetated or stripped and quiescent or exposed to wind to study transport at this important discharge boundary.

Preliminary experiments were conducted with methane as the source gas at the centreline of the base and Ottawa sand as the medium. Methane concentrations in the soil as % by volume after 68 and 92 minutes are shown in Figures 30 and 31 for one-half of the symmetrical box. No pressure gradient existed across the box from the source to the upper open discharge surface. The methane contours are consistent with transport by diffusion.

Eight flux box experiments were performed during the investigation, seven with the vapour source below the sand at the centre of the box and

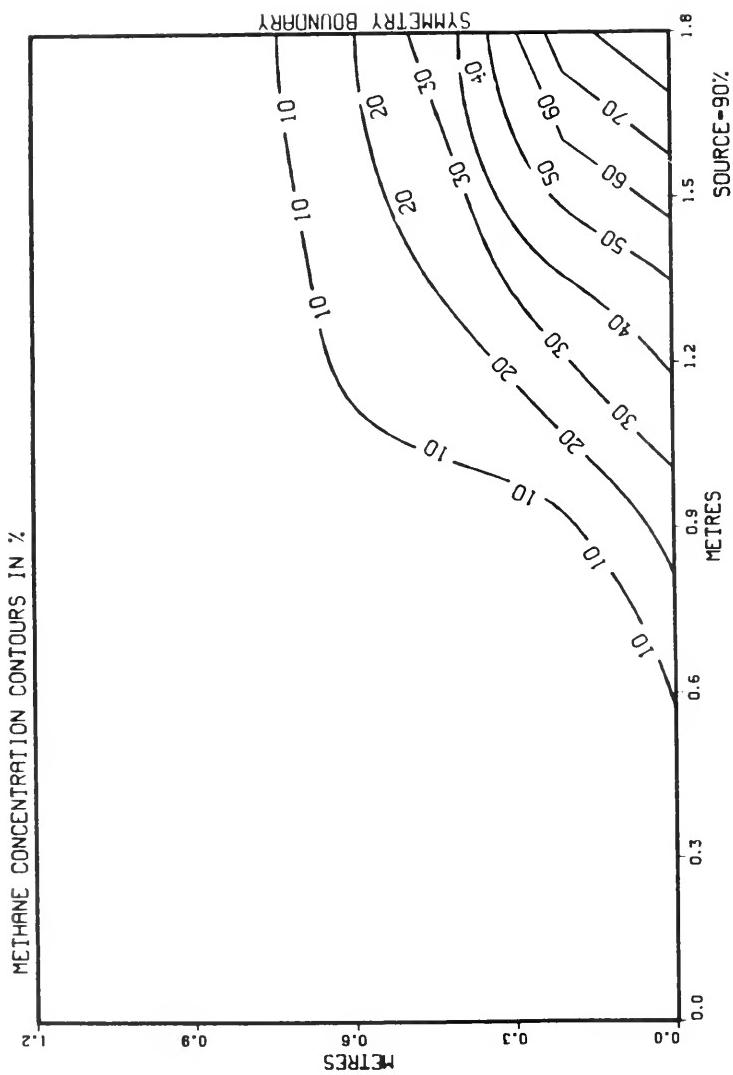


Figure 30 EXPERIMENT 1 - METHANE IN BOX
TIME = 68 MIN.

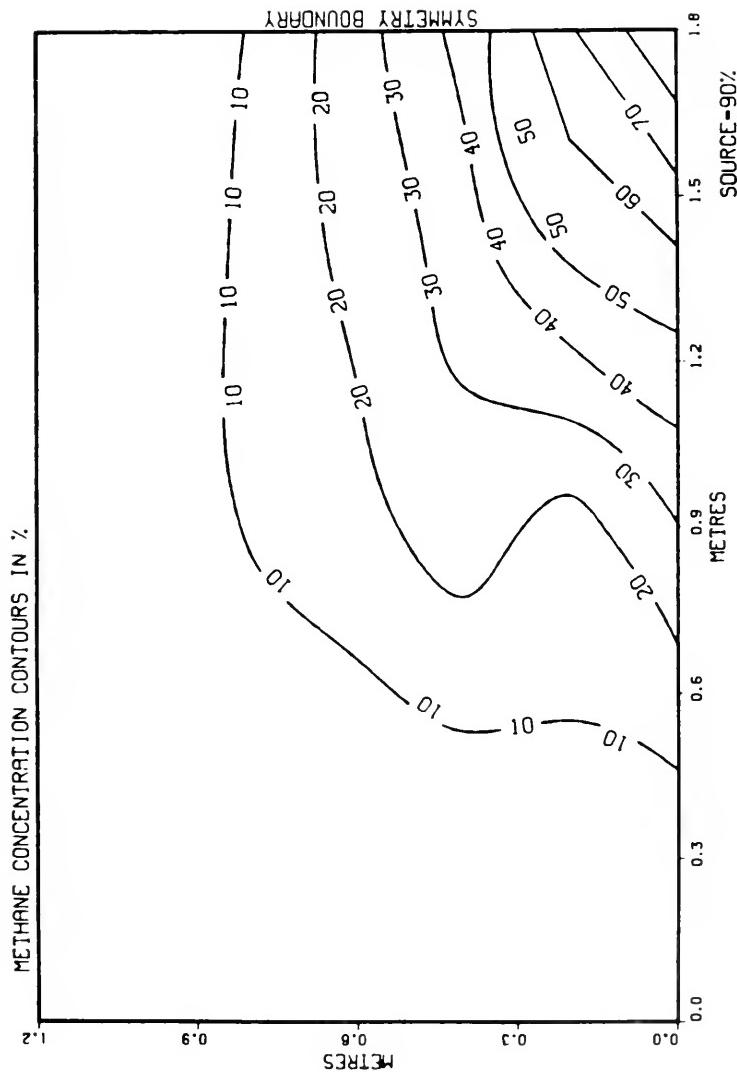


Figure 31 EXPERIMENT 1 - METHANE IN BOX
TIME = 92 MIN.

one with a vapour source located 45 cm below the surface of the sand. The following conditions were the same for all experiments.

- Maximum temperature variation within the soil was .5°C in response to changes of up to 5°C in room temperature outside the box.
- All experiments involved diffusion only. No pressure gradients between the source and the discharge surface could be detected.
- Daily atmosphere pressure variations were less than 5mm Hg.

The results of two experiments are presented here as examples of the work done.

Liquid Pentane as a Vapour Source at the Base

Liquid pentane at an average temperature of 23.5°C was placed as an open source at the base of the box. Vapours were allowed to enter the previously air filled soil for 75 hours. The vapour concentrations (% by volume) measured at 24 and 72 hours in the soil are presented as contours in Figure 32 for half of the box (symmetry assumed). The outward movement of the pentane vapours is shown in the comparison of the two graphs. Since pentane vapours are more dense than air, the upward motion was due entirely to diffusion with discharge occurring at the open soil surface. Measurements taken after 72 hours indicated that the contours had reached a nearly steady position. The concentration of pentane vapour in the soil immediately above the liquid source was approximately 18% by volume.

The Allan Model (Allan, 1985) was tested to determine whether or not it could successfully simulate the pentane data. The model consists of two dimensional, finite element solutions of the flow (Darcy Equation) and continuity equations. The boundary conditions and the

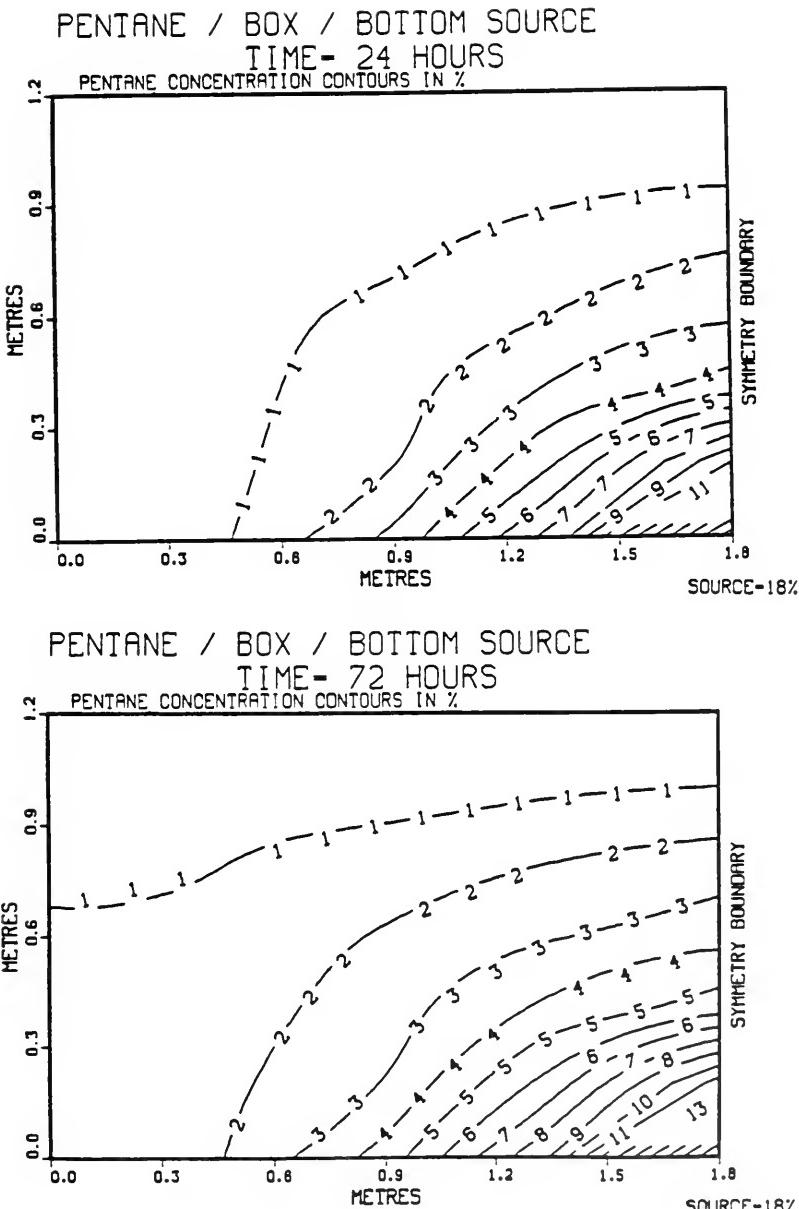


Figure 32 PENTANE EXPERIMENT WITH BOTTOM SOURCE

input parameters for the soil, air and pentane were those determined for the experiments themselves. Appropriate grid spacings and time steps were estimated but the model was not fitted to the data. The results of the simulations at 25 and 75 hours are shown in Figure 33. The comparison between these simulations and the actual data (Figure 32) is extremely good and provides verification that the model is capable of producing accurate simulations of vapour transport in two-dimensional soil configurations.

Other Vapours

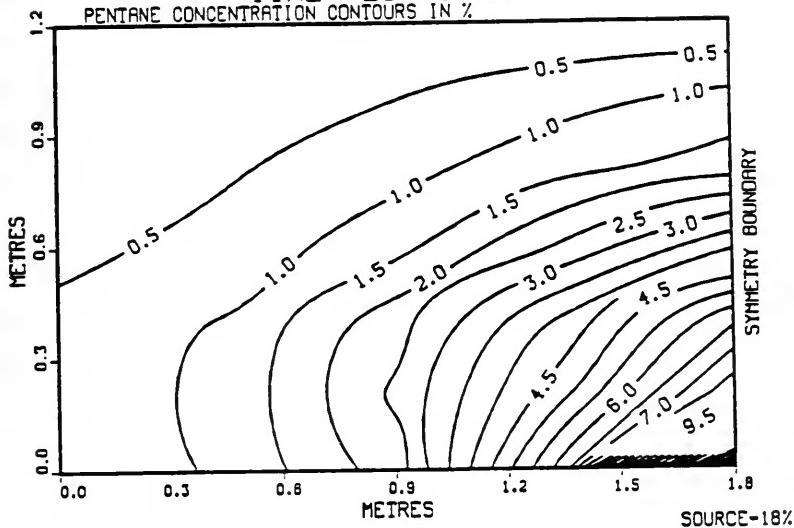
Similar experiments and simulations were performed using methane and liquid acetone as sources. The results from the methane work were of the same good quality as those presented for pentane. The acetone simulations did not match the experimental data however. They produced a more rapid migration than observed in the experimental data. It is known that polar vapours such as acetone tend to adsorb onto dry soils much more readily than nonpolar vapours like pentane.

Consequently, since this soil was very dry (0.935% H₂O dry wt), extensive adsorption of acetone is likely to have occurred. Although the Allan model has a component to allow for the introduction of adsorption, no isotherm data have been found to include in the simulations. As a result, no adsorption was included. Experiments are currently in progress to quantify acetone adsorption onto the experimental soil.

Pentane as a Vapour Source Suspended in the Soil

Experiments were performed where pentane vapour was introduced in the middle of the box. A teflon pipe with holes was inserted into the

PENTANE SIMULATION FOR THE BOX
TIME- 25 HOURS



PENTANE SIMULATION FOR THE BOX
TIME- 75 HOURS

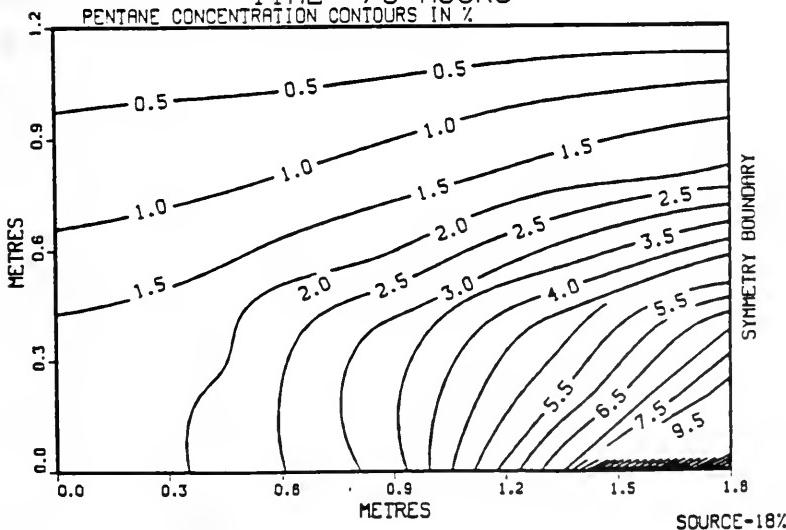


Figure 33 PENTANE SIMULATION FOR BOTTOM SOURCE

soil, 45 cm down from the open surface. A pentane vapour source was connected to this pipe. This then served as a suspended source for vapour migration. Measurements were then taken to detect pentane vapours throughout the soil regime. The data collected are presented in Figure 34. They show that the denser pentane vapours drifted downward due to both diffusion and body forces and then moved laterally at the sealed base of the box. Evidence of diffusion upward to the open soil surface is also provided by the vapour concentration contours.

The tendency observed here is that denser vapours can penetrate deeply into unsaturated soils and then move laterally at the water table or some poorly permeable stratum. This has major implication in field situations.

6. DISCUSSION

The research completed during this project studied the fundamentals of hazardous immiscible liquid movement in soil. It was considered necessary to adopt a somewhat theoretical approach because so little information about the processes involved was available. The research produced numerical simulation models for spill formation, liquid penetration into soil and vapour movement through soil. It also generated experimental data with which to observe the fundamental processes and to provide a basis against which to test the simulation models. The results summarized in this report show that the research has been successful in achieving most of its objectives and has contributed significantly to understanding and dealing with immiscible liquids in soil.

Because of limited time and resources, it was necessary to proceed

without examining a range of chemicals or soils or replicating significant numbers of experiments. Consequently, further work is required in this regard to expand and to verify the work completed to date.

It is also now necessary to extend the results of this project to other applications. The first of these should involve the application of the methods and models developed to field conditions for assessing remedial measures and for estimating further contaminant movement. Subsequent effort should be made to obtain data from other sources as it becomes available to corroborate the information obtained here.

The transfer of contaminants from the immiscible liquid phase to either the aqueous or the gaseous phases is a significant problem for which research is also required. This should include as a minimum, studying rates of contaminant phase transfer and the factors which affect them.

Future research in Civil Engineering at the University of Waterloo will be developed along these lines.

7. TECHNICAL REPORTS

The details of the research dealing with model development, experimentation and analysis of results are presented in the seven Technical Reports. These are either copies of graduate student theses or specially prepared reports describing the various phases of the work.

They include:

- TR1 COMBINED LITERATURE REVIEW.
- TR2 NUMERICAL MODELLING OF THE SPILL OF VOLATILE TOXIC LIQUIDS OVER POROUS MEDIA.
- TR3 MODELLING THE SPREADING, INFILTRATION AND EVAPORATION OF CHEMICAL SPILLS ON GRASS AND IMPERMEABLE SURFACES.
- TR4 NUMERICAL MODELLING OF IMMISCIBLE TWO-PHASE FLOW IN POROUS MEDIA.
- TR5 EXPERIMENTS ON THE MOVEMENT OF IMMISCIBLE LIQUIDS IN SOIL.
- TR6 MODELLING AND SENSITIVITY ANALYSIS OF VAPOUR MIGRATION IN SOIL FROM SPILLED VOLATILE LIQUIDS.
- TR7 EXPERIMENTS ON VOLATILIZATION AND VAPOUR TRANSPORT IN SOIL.

Each Report was supported either totally (TR1, TR2, TR5, TR6 and TR7) or in part (TR3 and TR4) with funding from the MOE. Technical Report TR3 describes work done in collaboration with S.L. Ross Environmental Research Limited in Ottawa and is a copy of a report from that firm. Technical Report TR4 is a copy of the M.A.Sc. Thesis prepared by M. Osborne under the supervision of Professor J.F. Sykes but supported in part by this project grant. All other Reports were prepared totally as the work of this project.

TR1 "COMBINED LITERATURE REVIEW" is presented in an accompanying report. Because of the volume of work contained in the other Reports, it was not possible to present them here as a complete set of documents. It was therefore necessary to provide this Technical Summary. However, copies of the Reports can be obtained by contacting:

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In order to assist the reader in selecting Technical Reports, the abstract from each Report is presented below.

TR2 NUMERICAL MODELLING OF THE SPILL OF VOLATILE TOXIC LIQUIDS OVER POROUS MEDIA

The research that is embodied in this thesis was undertaken to develop a model which can simulate the interaction of an accidentally-spilled liquid and the environment that it is contaminating. This research is primarily concerned with the spill of toxic, volatile liquids from ruptures in trains and truck tanks, and in the pipelines that are used to transport these liquids.

The equations, which represent one-dimensional radial spills, are developed. The processes of resistance to overland flow, evaporation, and infiltration are incorporated into these equations.

The solution domain includes: supercritical flow, a spontaneous hydraulic jump, subcritical flow and a moving bore, combined with a time-dependent inflow boundary. The explicit finite difference MacCormack scheme is used to numerically solve the spill equations.

The model parameters are estimated either by using known values, or from physically-based theory, for the spill of benzene. The spill model

is evaluated for spills under different environmental and inflow conditions.

TR3 MODELLING THE SPREADING, INFILTRATION AND EVAPORATION OF CHEMICAL SPILLS ON GRASS AND IMPERMEABLE SURFACES

Large scale spills were carried out in co-operation with the firm of S.L. Ross in Ottawa using both impermeable and sodded soil surfaces, either flat or inclined at 10°. Up to 200 L of liquids with viscosities ranging from 1 to 65 cp were spilled onto the various surfaces at rates ranging from 22 to 95 L·min⁻¹. A total of 27 experiments were completed. The data recorded with respect to time included bore and hydraulic jump locations, depths, runoff and infiltration.

The spills were simulated using the MBPF model with good fits produced. The model roughness coefficient (*n*) was used as a fitting parameter with values ranging from 0.005 for a painted surface to 1.75 for a sodded surface.

Both sets of spill experiments provided useful quantitative data about the spreading and infiltration of HIL spills in response to variations in fluid type, spill rate and receptor surface slope, roughness and permeability. Similar data from other sources were extremely limited prior to this work. The experiments also provided a data base from which spill models could be developed and tested.

TR4 NUMERICAL MODELLING OF IMMISCIBLE TWO-PHASE FLOW IN POROUS MEDIA

Mathematical simulation of two-phase flow in porous media has been used in the petroleum industry for some time, to analyze the behaviour of gas and oil in reservoirs, and to optimize the effects of steam- and water-flooding. Various numerical techniques, including the finite-difference and finite-element methods have been used to solve the

immiscible displacement equations. However, applications of such numerical models to immiscible groundwater contamination problems is a relatively new practice.

In this study, a two-dimensional, two-phase mathematical model has been developed, based on Darcy's law and conservation of mass for each liquid. The result is a pair of coupled, nonlinear partial differential equations which display both parabolic and hyperbolic characteristics, depending on the magnitude of a nonlinear coefficient.

A numerical model has been developed to solve the equations, which uses a generalized method of weighted residuals in conjunction with the finite-element method and linear quadrilateral isoparametric elements. To alleviate numerical difficulties associated with hyperbolic equations, upstream weighting of the spatial terms in the model has been incorporated.

The theoretical and numerical accuracy of the model has been verified by comparison of simulation results with those from an existing one-dimensional two-phase flow simulator.

The finite-element model has been applied to simulate the migration of an immiscible organic solvent in groundwater, from a chemical waste disposal site located north of Niagara Falls, New York. The effects of uncertainty regarding several of the liquid and porous media properties have been examined, and it is concluded that the value of the model is limited less by the numerical approximations involved than by the accuracy of input parameter estimation.

TR5 EXPERIMENTS ON THE MOVEMENT OF IMMISCIBLE LIQUIDS IN SOIL

Many liquids which are immiscible with water are of environmental concern because they pose a serious threat of groundwater contamination. There is little research on the movement of these hazardous liquids in soil.

In this thesis, capillary pressure, relative permeability, and immiscible displacement experiments were performed. The fluids used were immiscible and nonhazardous to allow for the safe development and refinement of the equipment and methods prior to using hazardous liquids.

The semi-permeable membrane method was chosen to measure the capillary pressure curves. Three capillary pressure versus saturation curves were measured.

Problems existed with the method because only part of the imbibition curve can be measured and because up to three months are required to measure a complete capillary pressure versus saturation curve but these are not major limitations. Overall, the semi-permeable should be a simple and effective way of measuring capillary pressure curves for hazardous immiscible liquids.

A steady-state method was chosen to measure a relative permeability curve. One relative permeability curve was measured but problems were encountered. To measure relative permeability curves for hazardous immiscible liquids, either the effect of high flowrates on the saturation measurement must be studied or a nonsteady state method or an estimation method used. Nonsteady methods and estimation methods are quicker and require less fluid but may not be as accurate.

The thermoprobe was developed for the nondestructive in situ

measurement of saturation. The thermoprobe consists of a small wire to which an electric current is applied. The electric current produces heat and raises the temperature of the fluid around the wire. The temperature rise depends on the specific heat and thermoconductivity of the fluid surrounding the wire and is measured to determine what fluid or mixture of fluids surround the wire.

A series of six vertical one-dimensional immiscible displacement experiments were performed to examine the shape of the front under different conditions. The thermoprobe was used to record the shape of the front. The front was always very sharp at its leading edge and more dispersed as pendular saturation was approached. This was not expected for experiments with the mixed sand which was well graded. The sharp front in the mixed sand was attributed to the higher head to capillary force ratio or gravity effects.

The thermoprobe functioned well during these experiments. The thermoprobe was able to detect the displacement front, make several readings as the front passed by, and showed little scatter in the readings during this time.

A two-dimensional experiment was performed using trichloroethylene. It illustrated the formation of 'fingers' and the movement of trichloroethylene around finer grain lenses.

The one-dimensional experiments were modelled numerically and analytically. The analytical model generally overpredicted the flux through the column.

The numerical model, WSTIF, was used to simulate the one-dimensional experiments. It performed better than the analytical model

in some simulations and worse in others. It was able to accurately predict the general shape of the displacement front.

TR6 MODELLING AND SENSITIVITY ANALYSIS OF VAPOUR MIGRATION IN SOIL FROM SPILLED VOLATILE LIQUIDS

The hazards of vapour releases from spilled and/or buried immiscible liquids have not been widely studied. It was felt that a model of the movement would be useful in order to examine the influence of various factors on the movement and to simulate field conditions to evaluate existing hazards and possible remedial measures. The scope of the physics and chemistry of the movement and the properties of common soil systems dictated that such a model must be numerical.

The model developed in this work is a two-dimensional finite element model of vapour migration from a stationary volatile liquid source in soil. It assumes a steady state flow field and has a noniterative solution. It has been verified with analytical solutions of one- and two-dimensional contaminant transport. Tests of the model with field data on methane movement partially verified its capabilities to replicate vapour movement in the field. Field data on actual vapour movement could not be found, so two test scenarios were developed. The results of the simulations based on these scenarios showed possible vapour migration patterns from two different source configurations. The model can also complete an adjoint sensitivity analysis of its results. The adjoint solution was verified by testing its predictions against actual results.

Sandbox-type experiments with different soils and different chemicals could be used to verify the model and to quantify different parameters. Monitoring programs at suspect waste sites should be

initiated to gather field data so that the model can be fully field-verified and some field properties can be determined.

TR7 EXPERIMENTS ON VOLATILIZATION AND VAPOUR TRANSPORT IN SOIL

Hazardous volatile organic compounds frequently contaminate soil. These compounds volatilize into the soil air and dissolve into groundwater. To determine the dangers caused by hazardous vapours it is necessary to understand the mechanisms involved in their movement in soil. Progress has been made in analytical modelling of vapour transport through soil. There is however, a lack of experimental data with which to validate proposed models and to understand vapour transport better.

Experimental methodologies were developed that measured vapour migration in soil under ambient conditions in one and two dimensions. Small column experiments provided data from which fundamental processes of vapour transport, such as molecular diffusion and density dependent flow, could be assessed. Larger vapour chamber experiments enabled contaminant vapours to migrate both horizontally and vertically. Heavy vapours showed a preference to spread laterally rather than migrate upwards when a bottom source was used. Molecular diffusion still caused considerable upward migration of heavy vapours.

A numerical finite element model was used to simulate the experimental data. It incorporated a transient pressure field solution that allowed advection caused by density differences to be simulated. The column experiments were simulated reasonably well although end boundary effects were evident. The vapour chamber simulations for pentane and methane experiments were excellent providing concentration profiles very close to those measured. Model simulation of a vapour

chamber experiment using acetone overpredicted the transient concentration distributions indicating that acetone vapour may have adsorbed onto the soil. An experiment to measure vapour phase adsorption was designed.

The results of this study indicated that advection caused by density gradients and molecular diffusion are the major mechanisms of vapour transport under ambient conditions. Further experiments incorporating variable water contents, adsorption and external pressure gradients would replicate field conditions more closely.

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